VOL. XXI. [FEBRUARY, 1899.] NO. 2.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

A NEW METHOD FOR THE DETERMINATION OF ZINC.

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Received October 22, 1898.

PRACTICALLY two methods only are in general use for the gravimetric determination of zinc. Of these, the carbonate method with its many imperfections is being displaced by the phosphate method, at least in this country.

With care the latter will yield excellent results. In our practice it is customary to use ammonium phosphate in place of the usual sodium salt,[1] and after the precipitation of the phosphate to destroy the slight excess of ammonia remaining after heating on the water-bath, by the cautious addition of dilute acetic acid. Under these conditions the filtrate is free from zinc.

Directly igniting the sulphide and filter, and weighing as oxide or sulphide, has been used, but is open to serious objection if the amount of zinc is at all large.

As far as we are aware no one has proposed the solution of the sulphide in nitric acid, the evaporation of the solution so obtained and the conversion of the residue to oxide by ignition. As a second precipitation and washing is avoided it is quicker than the carbonate or phosphate methods and is preferable to

[1] Garrigues : This Journal, 19, 934.

the latter in that the impurities almost invariably present in the zinc precipitate may be easily determined and allowed for.

The sample of ore for analysis (one-half to one gram according to its zinc content) is dissolved and the metals precipitated by hydrogen sulphide separated by the usual methods. After expelling hydrogen sulphide, the solution is colored by bromine water, and the iron and any manganese present are separated by ammonia. The precipitate is dissolved in hydrochloric acid and the precipitation is repeated a second or third time if necessary.

If the ore is one which is known to be free from lime and magnesia the combined filtrates may be boiled down immediately with the addition of an excess of nitric acid to destroy chlorides and ammonium salts. After the removal of the chlorine, the solution is transferred to a weighed platinum dish, evaporated to dryness, ignited and weighed as oxide.

The troublesome filtration and washing of the zinc sulphide should be avoided if possible. In our opinion better results are obtained by the ferrocyanide titration of the solution of the unwashed sulphide than by any gravimetric method involving the filtration and *washing* of this precipitate[1].

The zinc is best precipitated as follows: Acidulate the warm ammoniacal filtrate from the iron with hydrochloric acid, add a few drops of sulphurous acid to neutralize the bromine set free, then three or four drops of methyl orange.[2] Neutralize with ammonia carefully and add ammonium sulphide drop by drop with constant stirring until a drop of the solution gives a dark coloration with a drop of dilute ferric chloride solution on a porcelain plate, showing a slight excess only of ammonium sulphide. The liquid is now warmed on the water-bath until the sulphide has settled and is filtered through a double ribbed filter. Under these conditions a clear filtrate is invariably obtained, but if washing is attempted the filtrate is frequently cloudy.

[1] C. F. McKenna has suggested to the author that the addition of a little paper pulp to the solution prior to filtration will insure a clear filtrate. If some asbestos is stirred into a cloudy zinc filtrate and the solution passed again through the paper the filtrate will generally be clear. But in any case the slow washing of the precipitate exposes us to a loss through oxidation.

[2] The methyl orange used in exactly neutralizing the solution prior to the ferrocyanide titration and which slightly interferes with the delicacy of the end-reaction, may be readily destroyed after the acidulation by pouring into the beaker a little bromine vapor and stirring this in.

We therefore dissolve directly, without washing, in hot nitric acid (1 : 3) or in dilute hydrochloric acid if cobalt or nickel are present, and correct the weight of the oxide subsequently found for the small amounts of lime or magnesia present. It is well to make a qualitative test for these elements in the filtrate from the sulphide. If absent or in small amount the correction in the weight of the oxide may be omitted.

The solution is boiled down rapidly in a casserole with the addition of nitric acid to expel chlorides. When almost dry the contents are rinsed into a weighed platinum dish or crucible. The evaporation is continued on the water-bath or hot plate until dry, when the nitrate is ignited at the full heat of the Bunsen burner. As some zinc sulphate, which is always present, is not decomposed at this temperature, it is necessary to break up this compound by intense ignition over the blast-lamp. Any lumps should be first broken up by a blunt glass rod. Ammonium carbonate may be used but is liable to occasion some loss.

It may be possible, by igniting at a low heat, to weigh the zinc as sulphate, after evaporating with sulphuric acid. We are working on this now.

After weighing, the oxide is dissolved in hydrochloric acid and the small amount of iron always present thrown down with ammonia, ignited, brushed into the tared watch-glass in the balance and weighed directly. The filtrate is acidulated with hydrochloric acid, heated to boiling, and tested for sulphates with barium chloride. A slight precipitate will usually form but this may, in general, be neglected if the ignition has been properly performed. If in weighable amount it may be treated as in the case of the iron, calculated to sulphur trioxide, and together with the ferric oxide deducted from the weight of the impure oxide.

If lime or magnesia were present the filtrate from the iron should be divided into equal parts, one of which is tested for sulphates and the other for lime and magnesia by throwing out the zinc as sulphide, and testing the filtrate by the ordinary methods. As a rule this is unnecessary unless the lime or magnesia is present in large amounts, for the sulphide is precipitated in dilute solution and the amount of lime remaining in the unwashed sulphide would usually be very small.

The correction for impurities may seem tedious but in reality

it is quickly carried out. Richards has found that zinc oxide obtained by the ignition of the nitrate contains a little occluded nitrogen. This would only amount to a few tenths of a milligram and may be neglected unless unusually accurate work is called for.

For the determination of zinc in alloys containing copper, tin, lead, iron, and zinc, dissolve in nitric acid, evaporate to dryness, and take up with nitric acid if tin be present. Filter and separate copper and lead simultaneously by electrolysis. The solution should contain five to ten cc. concentrated nitric acid in 150 to 200 cc. water. After removing and washing the electrodes carrying copper and lead the solution is evaporated to dryness in a weighed platinum dish and the residue ignited and weighed. Dissolve in hydrochloric acid and separate the usually small amount of iron present by ammonia. Ignite, weigh, and deduct from the weight of the zinc oxide. If nickel be present the weight of the combined oxides may be taken and the nickel afterwards determined, when the zinc may be found by difference.

Zinc in pure spelters is best determined by difference. In impure samples it is sometimes more convenient and equally accurate to determine zinc directly. Dissolve one-half gram in nitric acid and separate the lead electrolytically in a solution carrying ten per cent. nitric acid. Use the platinum cylinder in this case to collect the lead peroxide. Evaporate the solution to dryness in a weighed dish, ignite, and weigh. Dissolve in a little hydrochloric acid, reduce with two to three grams granulated zinc, add sulphuric acid to complete the reaction, dilute with ice water to one liter, and titrate with permanganate. Correct for the amount of iron found. If cadmium, arsenic, or other impurities were present in more than traces the above method would be inapplicable unless modified to include treatment by hydrogen sulphide.

We have not found time to make an extended series of tests of this method but, in numerous analyses of ores and the complete analysis of alloys in which in duplicate analyses the zinc was determined by the well-known methods, the author has convinced himself of the accuracy of the method.

LABORATORY OF RICKETTS AND BANKS,
NEW YORK.

BAUMÉ'S HYDROMETER—AMERICAN STANDARD.

CALCULATED BY SIDNEY S. EMERY.

Received October 17, 1898.

FOR LIQUIDS HEAVIER THAN WATER, SP. GR. $= \frac{145}{145 - {}^{\circ}\text{Bé}}$ AT 60° F.

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
0.0	1.0000	.9	1.0276	.8	1.0569	.7	1.0878
.1	1.0007	4.0	1.0284	.9	1.0576	.8	1.0886
.2	1.0014	.1	1.0291	8.0	1.0584	.9	1.0894
.3	1.0021	.2	1.0298	.1	1.0592	12.0	1.0902
.4	1.0028	.3	1.0306	.2	1.0599	.1	1.0910
.5	1.0035	.4	1.0313	.3	1.0607	.2	1.0919
.6	1.0042	.5	1.0320	.4	1.0615	.3	1.0927
.7	1.0049	.6	1.0328	.5	1.0623	.4	1.0935
.8	1.0055	.7	1.0335	.6	1.0630	.5	1.0943
.9	1.0062	.8	1.0342	.7	1.0638	.6	1.0952
1.0	1.0069	.9	1.0350	.8	1.0646	.7	1.0960
.1	1.0076	5.0	1.0357	.9	1.0654	.8	1.0968
.2	1.0083	.1	1.0365	9.0	1.0662	.9	1.0977
.3	1.0090	.2	1.0372	.1	1.0670	13.0	1.0985
.4	1.0097	.3	1.0379	.2	1.0677	.1	1.0993
.5	1.0105	.4	1.0387	.3	1.0685	.2	1.1002
.6	1.0112	.5	1.0394	.4	1.0693	.3	1.1010
.7	1.0119	.6	1.0402	.5	1.0701	.4	1.1018
.8	1.0126	.7	1.0409	.6	1.0709	.5	1.1027
.9	1.0133	.8	1.0417	.7	1.0717	.6	1.1035
2.0	1.0140	.9	1.0424	.8	1.0725	.7	1.1043
.1	1.0147	6.0	1.0432	.9	1.0733	.8	1.1052
.2	1.0154	.1	1.0439	10.0	1.0741	.9	1.1060
.3	1.0161	.2	1.0447	.1	1.0749	14.0	1.1069
.4	1.0168	.3	1.0454	.2	1.0757	.1	1.1077
.5	1.0175	.4	1.0462	.3	1.0765	.2	1.1086
.6	1.0183	.5	1.0469	.4	1.0773	.3	1.1094
.7	1.0190	.6	1.0477	.5	1.0781	.4	1.1103
.8	1.0197	.7	1.0484	.6	1.0789	.5	1.1111
.9	1.0204	.8	1.0492	.7	1.0797	.6	1.1120
3.0	1.0211	.9	1.0500	.8	1.0805	.7	1.1128
.1	1.0218	7.0	1.0507	.9	1.0813	.8	1.1137
.2	1.0226	.1	1.0515	11.0	1.0821	.9	1.1145
.3	1.0233	.2	1.0522	.1	1.0829	15.0	1.1154
.4	1.0240	.3	1.0530	.2	1.0837	.1	1.1162
.5	1.0247	.4	1.0538	.3	1.0845	.2	1.1171
.6	1.0255	.5	1.0545	.4	1.0853	.3	1.1180
.7	1.0262	.6	1.0553	.5	1.0861	.4	1.1188
.8	1.0269	.7	1.0561	.6	1.0870	.5	1.1197

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.6	1.1206	.2	1.1619	.8	1.2063	.4	1.2543
.7	1.1214	.3	1.1628	.9	1.2073	.5	1.2554
.8	1.1223	.4	1.1637	25.0	1.2083	.6	1.2565
.9	1.1232	.5	1.1647	.1	1.2093	.7	1.2576
16.0	1.1240	.6	1.1656	.2	1.2104	.8	1.2587
.1	1.1249	.7	1.1665	.3	1.2114	.9	1.2598
.2	1.1258	.8	1.1675	.4	1.2124	30.0	1.2609
.3	1.1267	.9	1.1684	.5	1.2134	.1	1.2620
.4	1.1275	21.0	1.1694	.6	1.2144	.2	1.2631
.5	1.1284	.1	1.1703	.7	1.2154	.3	1.2642
.6	1.1293	.2	1.1712	.8	1.2164	.4	1.2653
.7	1.1302	.3	1.1722	.9	1.2175	.5	1.2664
.8	1.1310	.4	1.1731	26.0	1.2185	.6	1.2675
.9	1.1319	.5	1.1741	.1	1.2195	.7	1.2686
17.0	1.1328	.6	1.1750	.2	1.2205	.8	1.2697
.1	1.1337	.7	1.1760	.3	1.2216	.9	1.2708
.2	1.1346	.8	1.1769	.4	1.2226	31.0	1.2719
.3	1.1355	.9	1.1779	.5	1.2236	.1	1.2730
.4	1.1364	22.0	1.1789	.6	1.2247	.2	1.2742
.5	1.1373	.1	1.1798	.7	1.2257	.3	1.2753
.6	1.1381	.2	1.1808	.8	1.2267	.4	1.2764
.7	1.1390	.3	1.1817	.9	1.2278	.5	1.2775
.8	1.1399	.4	1.1827	27.0	1.2288	.6	1.2787
.9	1.1408	.5	1.1837	.1	1.2299	.7	1.2798
18.0	1.1417	.6	1.1846	.2	1.2309	.8	1.2809
.1	1.1426	.7	1.1856	.3	1.2319	.9	1.2821
.2	1.1435	.8	1.1866	.4	1.2330	32.0	1.2832
.3	1.1444	.9	1.1876	.5	1.2340	.1	1.2843
.4	1.1453	23.0	1.1885	.6	1.2351	.2	1.2855
.5	1.1462	.1	1.1895	.7	1.2361	.3	1.2866
.6	1.1472	.2	1.1905	.8	1.2372	.4	1.2877
.7	1.1481	.3	1.1915	.9	1.2383	.5	1.2889
.8	1.1490	.4	1.1924	28.0	1.2393	.6	1.2900
.9	1.1499	.5	1.1934	.1	1.2404	.7	1.2912
19.0	1.1508	.6	1.1944	.2	1.2414	.8	1.2923
.1	1.1517	.7	1.1954	.3	1.2425	.9	1.2935
.2	1.1526	.8	1.1964	.4	1.2436	33.0	1.2946
.3	1.1535	.9	1.1974	.5	1.2446	.1	1.2958
.4	1.1545	24.0	1.1983	.6	1.2457	.2	1.2970
.5	1.1554	.1	1.1993	.7	1.2468	.3	1.2981
.6	1.1563	.2	1.2003	.8	1.2478	.4	1.2993
.7	1.1572	.3	1.2013	.9	1.2489	.5	1.3004
.8	1.1581	.4	1.2023	29.0	1.2500	.6	1.3016
.9	1.1591	.5	1.2033	.1	1.2511	.7	1.3028
20.0	1.1600	.6	1.2043	.2	1.2522	.8	1.3040
.1	1.1609	.7	1.2053	.3	1.2532	.9	1.3051

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
34.0	1.3063	.6	1.3628	.2	1.4244	.8	1.4918
.1	1.3075	.7	1.3641	.3	1.4258	.9	1.4933
.2	1.3087	.8	1.3653	.4	1.4272	48.0	1.4948
.3	1.3098	.9	1.3666	.5	1.4286	.1	1.4964
.4	1.3110	39.0	1.3679	.6	1.4300	.2	1.4979
.5	1.3122	.1	1.3692	.7	1.4314	.3	1.4995
.6	1.3134	.2	1.3705	.8	1.4328	.4	1.5010
.7	1.3146	.3	1.3718	.9	1.4342	.5	1.5026
.8	1.3158	.4	1.3731	44.0	1.4356	.6	1.5041
.9	1.3170	.5	1.3744	.1	1.4371	.7	1.5057
35.0	1.3182	.6	1.3757	.2	1.4385	.8	1.5073
.1	1.3194	.7	1.3770	.3	1.4399	.9	1.5088
.2	1.3206	.8	1.3783	.4	1.4414	49.0	1.5104
.3	1.3218	.9	1.3796	.5	1.4428	.1	1.5120
.4	1.3230	40.0	1.3810	.6	1.4442	.2	1.5136
.5	1.3242	.1	1.3823	.7	1.4457	.3	1.5152
.6	1.3254	.2	1.3836	.8	1.4471	.4	1.5167
.7	1.3266	.3	1.3849	.9	1.4486	.5	1.5183
.8	1.3278	.4	1.3862	45.0	1.4500	.6	1.5199
.9	1.3291	.5	1.3876	.1	1.4515	.7	1.5215
36.0	1.3303	.6	1.3889	.2	1.4529	.8	1.5231
.1	1.3315	.7	1.3902	.3	1.4544	.9	1.5247
.2	1.3327	.8	1.3916	.4	1.4558	50.0	1.5263
.3	1.3339	.9	1.3929	.5	1.4573	.1	1.5279
.4	1.3352	41.0	1.3942	.6	1.4588	.2	1.5295
.5	1.3364	.1	1.3956	.7	1.4602	.3	1.5312
.6	1.3376	.2	1.3969	.8	1.4617	.4	1.5328
.7	1.3389	.3	1.3983	.9	1.4632	.5	1.5344
.8	1.3401	.4	1.3996	46.0	1.4646	.6	1.5360
.9	1.3414	.5	1.4010	.1	1.4661	.7	1.5376
37.0	1.3426	.6	1.4023	.2	1.4676	.8	1.5393
.1	1.3438	.7	1.4037	.3	1.4691	.9	1.5409
.2	1.3451	.8	1.4050	.4	1.4706	51.0	1.5426
.3	1.3463	.9	1.4064	.5	1.4721	.1	1.5442
.4	1.3476	42.0	1.4078	.6	1.4736	.2	1.5458
.5	1.3488	.1	1.4091	.7	1.4751	.3	1.5475
.6	1.3501	.2	1.4105	.8	1.4766	.4	1.5491
.7	1.3514	.3	1.4119	.9	1.4781	.5	1.5508
.8	1.3526	.4	1.4133	47.0	1.4796	.6	1.5525
.9	1.3539	.5	1.4146	.1	1.4811	.7	1.5541
38.0	1.3551	.6	1.4160	.2	1.4826	.8	1.5558
.1	1.3564	.7	1.4174	.3	1.4841	.9	1.5575
.2	1.3577	.8	1.4188	.4	1.4857	52.0	1.5591
.3	1.3590	.9	1.4202	.5	1.4872	.1	1.5608
.4	1.3602	43.0	1.4216	.6	1.4887	.2	1.5625
.5	1.3615	.1	1.4230	.7	1.4902	.3	1.5642

°Bé.	Sp. gr.
.4	1.5659
.5	1.5676
.6	1.5693
.7	1.5710
.8	1.5727
.9	1.5744
53.0	1.5761
.1	1.5778
.2	1.5795
.3	1.5812
.4	1.5830
.5	1.5847
.6	1.5864
.7	1.5882
.8	1.5899
.9	1.5917
54.0	1.5934
.1	1.5952
.2	1.5969
.3	1.5987
.4	1.6004
.5	1.6022
.6	1.6040
.7	1.6058
.8	1.6075
.9	1.6093
55.0	1.6111
.1	1.6129
.2	1.6147
.3	1.6165
.4	1.6183
.5	1.6201
.6	1.6219
.7	1.6237
.8	1.6256
.9	1.6274
56.0	1.6292
.1	1.6310
.2	1.6329
.3	1.6347
.4	1.6366
.5	1.6384
.6	1.6403
.7	1.6421
.8	1.6440
.9	1.6459
57.0	1.6477
.1	1.6496
.2	1.6515
.3	1.6534
.4	1.6553
.5	1.6571
.6	1.6590
.7	1.6609
.8	1.6628
.9	1.6648
58.0	1.6667
.1	1.6686
.2	1.6705
.3	1.6724
.4	1.6744
.5	1.6763
.6	1.6782
.7	1.6802
.8	1.6821
.9	1.6841
59.0	1.6860
.1	1.6880
.2	1.6900
.3	1.6919
.4	1.6939
.5	1.6959
.6	1.6979
.7	1.6999
.8	1.7019
.9	1.7039
60.0	1.7059
.1	1.7079
.2	1.7099
.3	1.7119
.4	1.7139
.5	1.7160
.6	1.7180
.7	1.7200
.8	1.7221
.9	1.7241
61.0	1.7262
.1	1.7282
.2	1.7303
.3	1.7324
.4	1.7344
.5	1.7365
.6	1.7386
.7	1.7407
.8	1.7428
.9	1.7449
62.0	1.7470
.1	1.7491
.2	1.7512
.3	1.7533
.4	1.7554
.5	1.7576
.6	1.7597
.7	1.7618
.8	1.7640
.9	1.7661
63.0	1.7683
.1	1.7705
.2	1.7726
.3	1.7748
.4	1.7770
.5	1.7791
.6	1.7813
.7	1.7835
.8	1.7857
.9	1.7879
64.0	1.7901
.1	1.7923
.2	1.7946
.3	1.7968
.4	1.7990
.5	1.8012
.6	1.8035
.7	1.8057
.8	1.8080
.9	1.8102
65.0	1.8125
.1	1.8148
.2	1.8170
.3	1.8193
.4	1.8216
.5	1.8239
.6	1.8262
.7	1.8285
.8	1.8308
.9	1.8331
66.0	1.8354
.1	1.8378
.2	1.8401
.3	1.8424
.4	1.8448
.5	1.8471
.6	1.8495
.7	1.8519
.8	1.8542
.9	1.8566
67.0	1.8590
.1	1.8614
.2	1.8638
.3	1.8662
.4	1.8686
.5	1.8710
.6	1.8734
.7	1.8758
.8	1.8782
.9	1.8807
68.0	1.8831
.1	1.8856
.2	1.8880
.3	1.8905
.4	1.8930
.5	1.8954
.6	1.8979
.7	1.9004
.8	1.9029
.9	1.9054
69.0	1.9079
.1	1.9104
.2	1.9129
.3	1.9155
.4	1.9180
.5	1.9205
.6	1.9231
.7	1.9256
.8	1.9282
.9	1.9308
70.0	1.9333

°Bé.	Sp. gr.
0	1.0000
1/8	1.0009
2/8	1.0017
3/8	1.0026
4/8	1.0035
5/8	1.0043
6/8	1.0052
7/8	1.0061
1	1.0069
1/8	1.0078
2/8	1.0087
3/8	1.0096
4/8	1.0105
5/8	1.0113
6/8	1.0122
7/8	1.0131
2	1.0140
1/8	1.0149
2/8	1.0158
3/8	1.0167
4/8	1.0175
5/8	1.0184
6/8	1.0193
7/8	1.0202
3	1.0211
1/8	1.0220
2/8	1.0229
3/8	1.0238
4/8	1.0247
5/8	1.0256
6/8	1.0265
7/8	1.0275
4	1.0284
1/8	1.0293
2/8	1.0302
3/8	1.0311
4/8	1.0320
5/8	1.0329
6/8	1.0339
7/8	1.0348
5	1.0357
1/8	1.0366
2/8	1.0376
3/8	1.0385
4/8	1.0394
5/8	1.0404
6/8	1.0413
7/8	1.0422
6	1.0432
1/8	1.0441
2/8	1.0450
3/8	1.0460
4/8	1.0469
5/8	1.0479
6/8	1.0488
7/8	1.0498
7	1.0507
1/8	1.0517
2/8	1.0526
3/8	1.0536
4/8	1.0545
5/8	1.0555
6/8	1.0565
7/8	1.0574
8	1.0584
1/8	1.0594
2/8	1.0603
3/8	1.0613
4/8	1.0623
5/8	1.0632
6/8	1.0642
7/8	1.0652
9	1.0662
1/8	1.0672
2/8	1.0681
3/8	1.0691
4/8	1.0701
5/8	1.0711
6/8	1.0721
7/8	1.0731
10	1.0741
1/8	1.0751
2/8	1.0761
3/8	1.0771
4/8	1.0781
5/8	1.0791
6/8	1.0801
7/8	1.0811
11	1.0821
1/8	1.0831
2/8	1.0841
3/8	1.0851
4/8	1.0861
5/8	1.0872
6/8	1.0882
7/8	1.0892
12	1.0902
1/8	1.0913
2/8	1.0923
3/8	1.0933
4/8	1.0943
5/8	1.0954
6/8	1.0964
7/8	1.0974
13	1.0985
1/8	1.0995
2/8	1.1006
3/8	1.1016
4/8	1.1027
5/8	1.1037
6/8	1.1048
7/8	1.1058
14	1.1069
1/8	1.1079
2/8	1.1090
3/8	1.1100
4/8	1.1111
5/8	1.1122
6/8	1.1132
7/8	1.1143
15	1.1154
1/8	1.1165
2/8	1.1175
3/8	1.1186
4/8	1.1197
5/8	1.1208
6/8	1.1219
7/8	1.1229
16	1.1240
1/8	1.1251
2/8	1.1262
3/8	1.1273
4/8	1.1284
5/8	1.1295
6/8	1.1306
7/8	1.1317
17	1.1328
1/8	1.1339
2/8	1.1350
3/8	1.1361
4/8	1.1373
5/8	1.1384
6/8	1.1395
7/8	1.1406
18	1.1417
1/8	1.1428
2/8	1.1440
3/8	1.1451
4/8	1.1462
5/8	1.1474
6/8	1.1485
7/8	1.1496
19	1.1508
1/8	1.1519
2/8	1.1531
3/8	1.1542
4/8	1.1554
5/8	1.1565
6/8	1.1577
7/8	1.1588
20	1.1600
1/8	1.1612
2/8	1.1623
3/8	1.1635
4/8	1.1647
5/8	1.1658
6/8	1.1670
7/8	1.1682
21	1.1694
1/8	1.1705
2/8	1.1717
3/8	1.1729
4/8	1.1741
5/8	1.1753
6/8	1.1765
7/8	1.1777
22	1.1789
1/8	1.1801
2/8	1.1813
3/8	1.1825
4/8	1.1837
5/8	1.1849
6/8	1.1861
7/8	1.1873

°Bé.	Sp. gr.
23	1.1885
1/8	1.1897
2/8	1.1910
3/8	1.1922
4/8	1.1934
5/8	1.1946
6/8	1.1959
7/8	1.1971
24	1.1983
1/8	1.1996
2/8	1.2008
3/8	1.2021
4/8	1.2033
5/8	1.2046
6/8	1.2058
7/8	1.2071
25	1.2083
1/8	1.2096
2/8	1.2109
3/8	1.2121
4/8	1.2134
5/8	1.2147
6/8	1.2159
7/8	1.2172
26	1.2185
1/8	1.2198
2/8	1.2211
3/8	1.2223
4/8	1.2236
5/8	1.2249
6/8	1.2262
7/8	1.2275
27	1.2288
1/8	1.2301
2/8	1.2314
3/8	1.2327
4/8	1.2340
5/8	1.2354
6/8	1.2367
7/8	1.2380
28	1.2393
1/8	1.2406
2/8	1.2420
3/8	1.2433
4/8	1.2446
5/8	1.2460
6/8	1.2473
7/8	1.2487
29	1.2500
1/8	1.2513
2/8	1.2527
3/8	1.2541
4/8	1.2554
5/8	1.2568
6/8	1.2581
7/8	1.2595
30	1.2609
1/8	1.2622
2/8	1.2636
3/8	1.2650
4/8	1.2664
5/8	1.2678
6/8	1.2691
7/8	1.2705
31	1.2719
1/8	1.2733
2/8	1.2747
3/8	1.2761
4/8	1.2775
5/8	1.2789
6/8	1.2804
7/8	1.2818
32	1.2832
1/8	1.2846
2/8	1.2860
3/8	1.2875
4/8	1.2889
5/8	1.2903
6/8	1.2918
7/8	1.2932
33	1.2946
1/8	1.2961
2/8	1.2975
3/8	1.2990
4/8	1.3004
5/8	1.3019
6/8	1.3034
7/8	1.3048
34	1.3063
1/8	1.3078
2/8	1.3093
3/8	1.3107
4/8	1.3122
5/8	1.3137
6/8	1.3152
7/8	1.3167
35	1.3182
1/8	1.3197
2/8	1.3212
3/8	1.3227
4/8	1.3242
5/8	1.3257
6/8	1.3272
7/8	1.3288
36	1.3303
1/8	1.3318
2/8	1.3333
3/8	1.3349
4/8	1.3364
5/8	1.3379
6/8	1.3395
7/8	1.3410
37	1.3426
1/8	1.3441
2/8	1.3457
3/8	1.3473
4/8	1.3488
5/8	1.3504
6/8	1.3520
7/8	1.3536
38	1.3551
1/8	1.3567
2/8	1.3583
3/8	1.3599
4/8	1.3615
5/8	1.3631
6/8	1.3647
7/8	1.3663
39	1.3679
1/8	1.3695
2/8	1.3712
3/8	1.3728
4/8	1.3744
5/8	1.3760
6/8	1.3777
7/8	1.3793
40	1.3810
1/8	1.3826
2/8	1.3843
3/8	1.3859
4/8	1.3876
5/8	1.3892
6/8	1.3909
7/8	1.3926
41	1.3942
1/8	1.3959
2/8	1.3976
3/8	1.3993
4/8	1.4010
5/8	1.4027
6/8	1.4044
7/8	1.4061
42	1.4078
1/8	1.4095
2/8	1.4112
3/8	1.4129
4/8	1.4146
5/8	1.4164
6/8	1.4181
7/8	1.4198
43	1.4216
1/8	1.4233
2/8	1.4251
3/8	1.4268
4/8	1.4286
5/8	1.4303
6/8	1.4321
7/8	1.4339
44	1.4356
1/8	1.4374
2/8	1.4392
3/8	1.4410
4/8	1.4428
5/8	1.4446
6/8	1.4464
7/8	1.4482
45	1.4500
1/8	1.4518
2/8	1.4537
3/8	1.4555
4/8	1.4573
5/8	1.4591
6/8	1.4610
7/8	1.4628

°Bé.	Sp. gr.
46	1.4646
1/8	1.4665
2/8	1.4684
3/8	1.4702
4/8	1.4721
5/8	1.4739
6/8	1.4758
7/8	1.4777
47	1.4796
1/8	1.4815
2/8	1.4834
3/8	1.4853
4/8	1.4872
5/8	1.4891
6/8	1.4910
7/8	1.4929
48	1.4948
1/8	1.4968
2/8	1.4987
3/8	1.5006
4/8	1.5026
5/8	1.5045
6/8	1.5065
7/8	1.5085
49	1.5104
1/8	1.5124
2/8	1.5144
3/8	1.5163
4/8	1.5183
5/8	1.5203
6/8	1.5223
7/8	1.5243
50	1.5263
1/8	1.5283
2/8	1.5303
3/8	1.5324
4/8	1.5344
5/8	1.5364
6/8	1.5385
7/8	1.5405
51	1.5426
1/8	1.5446
2/8	1.5467
3/8	1.5487
4/8	1.5508
5/8	1.5529
6/8	1.5550
7/8	1.5570
52	1.5591
1/8	1.5612
2/8	1.5633
3/8	1.5655
4/8	1.5676
5/8	1.5697
6/8	1.5718
7/8	1.5739
53	1.5761
1/8	1.5782
2/8	1.5804
3/8	1.5825
4/8	1.5847
5/8	1.5869
6/8	1.5890
7/8	1.5912
54	1.5934
1/8	1.5956
2/8	1.5978
3/8	1.6000
4/8	1.6022
5/8	1.6044
6/8	1.6066
7/8	1.6089
55	1.6111
1/8	1.6134
2/8	1.6156
3/8	1.6179
4/8	1.6201
5/8	1.6224
6/8	1.6246
7/8	1.6269
56	1.6292
1/8	1.6315
2/8	1.6338
3/8	1.6361
4/8	1.6384
5/8	1.6407
6/8	1.6431
7/8	1.6454
57	1.6477
1/8	1.6501
2/8	1.6524
3/8	1.6548
4/8	1.6571
5/8	1.6595
6/8	1.6619
7/8	1.6643
58	1.6667
1/8	1.6691
2/8	1.6715
3/8	1.6739
4/8	1.6763
5/8	1.6787
6/8	1.6812
7/8	1.6836
59	1.6860
1/8	1.6885
2/8	1.6910
3/8	1.6934
4/8	1.6959
5/8	1.6984
6/8	1.7009
7/8	1.7034
60	1.7059
1/8	1.7084
2/8	1.7109
3/8	1.7134
4/8	1.7160
5/8	1.7185
6/8	1.7211
7/8	1.7236
61	1.7262
1/8	1.7288
2/8	1.7313
3/8	1.7339
4/8	1.7365
5/8	1.7391
6/8	1.7417
7/8	1.7444
62	1.7470
1/8	1.7496
2/8	1.7523
3/8	1.7549
4/8	1.7576
5/8	1.7602
6/8	1.7629
7/8	1.7656
63	1.7683
1/8	1.7710
2/8	1.7737
3/8	1.7764
4/8	1.7791
5/8	1.7819
6/8	1.7846
7/8	1.7874
64	1.7901
1/8	1.7929
2/8	1.7957
3/8	1.7984
4/8	1.8012
5/8	1.8040
6/8	1.8069
7/8	1.8097
65	1.8125
1/8	1.8153
2/8	1.8182
3/8	1.8210
4/8	1.8239
5/8	1.8268
6/8	1.8297
7/8	1.8325
66	1.8354
1/8	1.8383
2/8	1.8413
3/8	1.8442
4/8	1.8471
5/8	1.8501
6/8	1.8530
7/8	1.8560
67	1.8590
1/8	1.8620
2/8	1.8650
3/8	1.8680
4/8	1.8710
5/8	1.8740
6/8	1.8770
7/8	1.8801
68	1.8831
1/8	1.8862
2/8	1.8893
3/8	1.8923
4/8	1.8954
5/8	1.8985
6/8	1.9016
7/8	1.9048

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
69	1.9079	$\frac{3}{8}$	1.9174	$\frac{5}{8}$	1.9237	$\frac{7}{8}$	1.9301
$\frac{1}{8}$	1.9110	$\frac{4}{8}$	1.9205	$\frac{6}{8}$	1.9269	70	1.9333
$\frac{2}{8}$	1.9142						

FOR LIQUIDS LIGHTER THAN WATER, SP. GR. $= \frac{140}{130 + {}^{\circ}\text{Bé}}$ AT 60° F.

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
10.0	1.0000	.9	0.9729	.8	0.9472	.7	0.9229
.1	0.9993	14.0	0.9722	.9	0.9466	.8	0.9223
.2	0.9986	.1	0.9715	18.0	0.9459	.9	0.9217
.3	0.9979	.2	0.9709	.1	0.9453	22.0	0.9211
.4	0.9972	.3	0.9702	.2	0.9447	.1	0.9204
.5	0.9964	.4	0.9695	.3	0.9440	.2	0.9198
.6	0.9957	.5	0.9689	.4	0.9434	.3	0.9192
.7	0.9950	.6	0.9682	.5	0.9428	.4	0.9186
.8	0.9943	.7	0.9675	.6	0.9421	.5	0.9180
.9	0.9936	.8	0.9669	.7	0.9415	.6	0.9174
11.0	0.9929	.9	0.9662	.8	0.9409	.7	0.9168
.1	0.9922	15.0	0.9655	.9	0.9402	.8	0.9162
.2	0.9915	.1	0.9649	19.0	0.9396	.9	0.9156
.3	0.9908	.2	0.9642	.1	0.9390	23.0	0.9150
.4	0.9901	.3	0.9635	.2	0.9383	.1	0.9144
.5	0.9894	.4	0.9629	.3	0.9377	.2	0.9138
.6	0.9887	.5	0.9622	.4	0.9371	.3	0.9132
.7	0.9880	.9	0.9615	.5	0.9365	.4	0.9126
.8	0.9873	.7	0.9609	.6	0.9358	.5	0.9121
.9	0.9866	.8	0.9602	.7	0.9352	.6	0.9115
12.0	0.9859	.9	0.9596	.8	0.9346	.7	0.9109
.1	0.9852	16.0	0.9589	.9	0.9340	.8	0.9103
.2	0.9845	.1	0.9582	20.0	0.9333	.9	0.9097
.3	0.9838	.2	0.0576	.1	0.9327	24.0	0.9091
.4	0.9831	.3	0.9569	.2	0.9321	.1	0.9085
.5	0.9825	.4	0.9563	.3	0.9315	.2	0.9079
.6	0.9818	.5	0.9556	.4	0.9309	.3	0.9073
.7	0.9811	.6	0.9550	.5	0.9302	.4	0.9067
.8	0.9804	.7	0.9543	.6	0.9296	.5	0.9061
.9	0.9797	.8	0.9537	.7	0.9290	.6	0.9056
13.0	0.9790	.9	0.9530	.8	0.9284	.7	0.9050
.1	0.9783	17.0	0.9524	.9	0.9278	.8	0.9044
.2	0.9777	.1	0.9517	21.0	0.9272	.9	0.9038
.3	0.9770	.2	0.9511	.1	0.9265	25.0	0.9032
.4	0.9763	.3	0.9504	.2	0.9259	.1	0.9026
.5	0.9756	.4	0.9498	.3	0.9253	.2	0.9021
.6	0.9749	.5	0.9492	.4	0.9247	.3	0.9015
.7	0.9743	.6	0.9485	.5	0.9241	.4	0.9009
.8	0.9736	.7	0.9479	.6	0.9235	.5	0.9003

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.6	0.8997	.2	0.8739	.8	0.8495	.4	0.8264
.7	0.8992	.3	0.8734	.9	0.8490	.5	0.8260
.8	0.8986	.4	0.8728	35.0	0.8485	.6	0.8255
.9	0.8980	.5	0.8723	.1	0.8480	.7	0.8250
26.0	0.8974	.6	0.8717	.2	0.8475	.8	0.8245
.1	0.8969	.7	0.8712	.3	0.8469	.9	0.8240
.2	0.8963	.8	0.8706	.4	0.8464	40.0	0.8235
.3	0.8957	.9	0.8701	.5	0.8459	.1	0.8230
.4	0.8951	31.0	0.8696	.6	0.8454	.2	0.8226
.5	0.8946	.1	0.8690	.7	0.8449	.3	0.8221
.6	0.8940	.2	0.8685	.8	0.8444	.4	0.8216
.7	0.8934	.3	0.8679	.9	0.8439	.5	0.8211
.8	0.8929	.4	0.8674	36.0	0.8434	.6	0.8206
.9	0.8923	.5	0.8669	.1	0.8429	.7	0.8202
27.0	0.8917	.6	0.8663	.2	0.8424	.8	0.8197
.1	0.8912	.7	0.8658	.3	0.8418	.9	0.8192
.2	0.8906	.8	0.8653	.4	0.8413	41.0	0.8187
.3	0.8900	.9	0.8647	.5	0.8408	.1	0.8182
.4	0.8895	32.0	0.8642	.6	0.8403	.2	0.8178
.5	0.8889	.1	0.8637	.7	0.8398	.3	0.8173
.6	0.8883	.2	0.8631	.8	0.8393	.4	0.8168
.7	0.8878	.3	0.8626	.9	0.8388	.5	0.8163
.8	0.8872	.4	0.8621	37.0	0.8383	.6	0.8159
.9	0.8866	.5	0.8615	.1	0.8378	.7	0.8154
28.0	0.8861	.6	0.8610	.2	0.8373	.8	0.8149
.1	0.8855	.7	0.8605	.3	0.8368	.9	0.8144
.2	0.8850	.8	0.8600	.4	0.8363	42.0	0.8140
.3	0.8844	.9	0.8594	.5	0.8358	.1	0.8135
.4	0.8838	33.0	0.8589	.6	0.8353	.2	0.8130
.5	0.8833	.1	0.8584	.7	0.8348	.3	0.8125
.6	0.8821	.2	0.8578	.8	0.8343	.4	0.8121
.7	0.8822	.3	0.8573	.9	0.8338	.5	0.8116
.8	0.8816	.4	0.8568	38.0	0.8333	.6	0.8111
.9	0.8811	.5	0.8563	.1	0.8328	.7	0.8107
29.0	0.8805	.6	0.8557	.2	0.8323	.8	0.8102
.1	0.8799	.7	0.8552	.3	0.8318	.9	0.8097
.2	0.8794	.8	0.8547	.4	0.8314	43.0	0.8092
.3	0.8788	.9	0.8542	.5	0.8309	.1	0.8088
.4	0.8783	34.0	0.8537	.6	0.8304	.2	0.8083
.5	0.8777	.1	0.8531	.7	0.8299	.3	0.8078
.6	0.8772	.2	0.8526	.8	0.8294	.4	0.8074
.7	0.8766	.3	0.8521	.9	0.8289	.5	0.8069
.8	0.8761	.4	0.8516	39.0	0.8284	.6	0.8065
.9	0.8755	.5	0.8511	.1	0.8279	.7	0.8060
30.0	0.8750	.6	0.8505	.2	0.8274	.8	0.8055
.1	0.8745	.7	0.8500	.3	0.8269	.9	0.8051

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
44.0	0.8046	.6	0.7839	.2	0.7642	.8	0.7455
.1	0.8041	.7	0.7834	.3	0.7638	.9	0.7451
.2	0.8037	.8	0.7830	.4	0.7634	58.0	0.7447
.3	0.8032	.9	0.7826	.5	0.7629	.1	0.7443
.4	0.8028	49.0	0.7821	.6	0.7625	.2	0.7439
.5	0.8023	.1	0.7817	.7	0.7621	.3	0.7435
.6	0.8018	.2	0.7812(5)	.8	0.7617	.4	0.7431
.7	0.8014	.3	0.7808	.9	0.7613	.5	0.7427
.8	0.8009	.4	0.7804	54.0	0.7609	.6	0.7423
.9	0.8005	.5	0.7799	.1	0.7605	.7	0.7419
45.0	0.8000	.6	0.7795	.2	0.7600	.8	0.7415
.1	0.7995	.7	0.7791	.3	0.7596	.9	0.7411
.2	0.7991	.8	0.7786	.4	0.7592	59.0	0.7407
.3	0.7986	.9	0.7782	.5	0.7588	.1	0.7403
.4	0.7982	50.0	0.7778	.6	0.7584	.2	0.7400
.5	0.7977	.1	0.7773	.7	0.7580	.3	0.7396
.6	0.7973	.2	0.7769	.8	0.7576	.4	0.7392
.7	0.7968	.3	0.7765	.9	0.7572	.5	0.7388
.8	0.7964	.4	0.7761	55.0	0.7568	.6	0.7384
.9	0.7959	.5	0.7756	.1	0.7563	.7	0.7380
46.0	0.7955	.6	0.7752	.2	0.7559	.8	0.7376
.1	0.7950	.7	0.7748	.3	0.7555	.9	0.7372
.2	0.7946	.8	0.7743	.4	0.7551	60.0	0.7368
.3	0.7941	.9	0.7739	.5	0.7547	.1	0.7365
.4	0.7937	51.0	0.7735	.6	0.7543	.2	0.7361
.5	0.7932	.1	0.7731	.7	0.7539	.3	0.7357
.6	0.7928	.2	0.7726	.8	0.7535	.4	0.7353
.7	0.7923	.3	0.7722	.9	0.7531	.5	0.7349
.8	0.7919	.4	0.7718	56.0	0.7527	.8	0.7345
.9	0.7914	.5	0.7713	.1	0.7523	.7	0.7341
47.0	0.7910	.6	0.7709	.2	0.7519	.8	0.7338
.1	0.7905	.7	0.7705	.3	0.7515	.9	0.7334
.2	0.7901	.8	0.7701	.4	0.7511	61.0	0.7330
.3	0.7896	.9	0.7697	.5	0.7507	.1	0.7326
.4	0.7892	52.0	0.7692	.6	0.7503	.2	0.7322
.5	0.7887	.1	0.7688	.7	0.7499	.3	0.7318
.6	0.7883	.2	0.7684	.8	0.7495	.4	0.7315
.7	0.7878	.3	0.7680	.9	0.7491	.5	0.7311
.8	0.7874	.4	0.7675	57.0	0.7487	.6	0.7307
.9	0.7870	.5	0.7671	.1	0.7483	.7	0.7303
48.0	0.7865	.6	0.7667	.2	0.7479	.8	0.7299
.1	0.7861	.7	0.7663	.3	0.7475	.9	0.7295
.2	0.7856	.8	0.7659	.4	0.7471	62.0	0.7292
.3	0.7852	.9	0.7654	.5	0.7467	.1	0.7288
.4	0.7848	53.0	0.7650	.6	0.7463	.2	0.7284
.5	0.7843	.1	0.7646	.7	0.7459	.3	0.7280

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.4	0.7277	.9	0.7110	.3	0.6955	.7	0.6806
.5	0.7273	67.0	0.7107	.4	0.6951	.8	0.6803
.6	0.7269	.1	0.7103	.5	0.6948	.9	0.6799
.7	0.7265	.2	0.7099	.6	0.6944	76.0	0.6796
.8	0.7261	.3	0.7096	.7	0.6941	.1	0.6793
.9	0.7258	.4	0.7092	.8	0.6938	.2	0.6790
63.0	0.7254	.5	0.7089	.9	0.6934	.3	0.6786
.1	0.7250	.6	0.7085	72.0	0.6931	.4	0.6783
.2	0.7246	.7	0.7081	.1	0.6927	.5	0.6780
.3	0.7243	.8	0.7078	.2	0.6924	.6	0.6776
.4	0.7239	.9	0.7074	.3	0.6920	.7	0.6773
.5	0.7235	68.0	0.7071	.4	0.6917	.8	0.6770
.6	0.7231	.1	0.7067	.5	0.6914	.9	0.6767
.7	0.7228	.2	0.7064	.6	0.6910	77.0	0.6763
.8	0.7224	.3	0.7060	.7	0.6907	.1	0.6760
.9	0.7220	.4	0.7056	.8	0.6903	.2	0.6757
64.0	0.7216	.5	0.7053	.9	0.6900	.3	0.6753
.1	0.7213	.6	0.7049	73.0	0.6897	.4	0.6750
.2	0.7209	.7	0.7046	.1	0.6893	.5	0.6747
.3	0.7205	.8	0.7042	.2	0.6890	.6	0.6744
.4	0.7202	.9	0.7039	.3	0.6886	.7	0.6740
.5	0.7198	69.0	0.7035	.4	0.6883	.8	0.6737
.6	0.7194	.1	0.7032	.5	0.6880	.9	0.6734
.7	0.7191	.2	0.7028	.6	0.6876	78.0	0.6731
.8	0.7187	.3	0.7025	.7	0.6873	.1	0.6728
.9	0.7183	.4	0.7021	.8	0.6869	.2	0.6724
65.0	0.7179	.5	0.7018	.9	0.6866	.3	0.6721
.1	0.7176	.6	0.7014	74.0	0.6863	.4	0.6718
.2	0.7172	.7	0.7011	.1	0.6859	.5	0.6715
.3	0.7168	.8	0.7007	.2	0.6856	.6	0.6711
.4	0.7165	.9	0.7004	.3	0.6853	.7	0.6708
.5	0.7161	70.0	0.7000	.4	0.6849	.8	0.6705
.6	0.7157	.1	0.6997	.5	0.6846	.9	0.6702
.7	0.7154	.2	0.6993	.6	0.6843	79.0	0.6699
.8	0.7150	.3	0.6990	.7	0.6839	.1	0.6695
.9	0.7147	.4	0.6986	.8	0.6836	.2	0.6692
66.0	0.7143	.5	0.6983	.9	0.6833	.3	0.6689
.1	0.7139	.6	0.6979	75.0	0.6829	.4	0.6686
.2	0.7136	.7	0.6976	.1	0.6826	.5	0.6683
.3	0.7132	.8	0.6972	.2	0.6823	.5	0.6679
.4	0.7128	.9	0.6969	.3	0.6819	.7	0.6676
.5	0.7125	71.0	0.6965	.4	0.6816	.8	0.6673
.6	0.7121	.1	0.6962	.5	0.6813	.9	0.6670
.7	0.7117	.2	0.6958	.6	0.6809	80.0	0.6667
.8	0.7114						

°Bé.	Sp. gr.
10	1.0000
1/8	0.9991
2/8	0.9982
3/8	0.9973
4/8	0.9964
5/8	0.9956
6/8	0.9947
7/8	0.9938
11	0.9929
1/8	0.9920
2/8	0.9912
3/8	0.9903
4/8	0.9894
5/8	0.9885
6/8	0.9877
7/8	0.9868
12	0.9859
1/8	0.9850
2/8	0.9842
3/8	0.9833
4/8	0.9825
5/8	0.9816
6/8	0.9807
7/8	0.9799
13	0.9790
1/8	0.9782
2/8	0.9773
3/8	0.9765
4/8	0.9756
5/8	0.9748
6/8	0.9739
7/8	0.9731
14	0.9722
1/8	0.9714
2/8	0.9706
3/8	0.9697
4/8	0.9689
5/8	0.9680
6/8	0.9672
7/8	0.9664
15	0.9655
1/8	0.9647
2/8	0.9639
3/8	0.9630
4/8	0.9622
5/8	0.9614
6/8	0.9605
7/8	0.9597
16	0.9589
1/8	0.9581
2/8	0.9573
3/8	0.9564
4/8	0.9556
5/8	0.9548
6/8	0.9540
7/8	0.9532
17	0.9524
1/8	0.9516
2/8	0.9508
3/8	0.9500
4/8	0.9492
5/8	0.9483
6/8	0.9475
7/8	0.9467
18	0.9459
1/8	0.9451
2/8	0.9444
3/8	0.9436
4/8	0.9428
5/8	0.9420
6/8	0.9412
7/8	0.9404
19	0.9396
1/8	0.9388
2/8	0.9380
3/8	0.9372
4/8	0.9365
5/8	0.9357
6/8	0.9349
7/8	0.9341
20	0.9333
1/8	0.9326
2/8	0.9318
3/8	0.9310
4/8	0.9302
5/8	0.9295
6/8	0.9287
7/8	0.9279
21	0.9272
1/8	0.9264
2/8	0.9256
3/8	0.9249
4/8	0.9241
5/8	0.9233
6/8	0.9226
7/8	0.9218
22	0.9211
1/8	0.9203
2/8	0.9195
3/8	0.9188
4/8	0.9180
5/8	0.9173
6/8	0.9165
7/8	0.9158
23	0.9150
1/8	0.9143
2/8	0.9135
3/8	0.9128
4/8	0.9121
5/8	0.9113
6/8	0.9106
7/8	0.9098
24	0.9091
1/8	0.9084
2/8	0.9076
3/8	0.9069
4/8	0.9061
5/8	0.9054
6/8	0.9047
7/8	0.9040
25	0.9032
1/8	0.9025
2/8	0.9018
3/8	0.9010
4/8	0.9003
5/8	0.8996
6/8	0.8989
7/8	0.8982
26	0.8974
1/8	0.8967
2/8	0.8960
3/8	0.8953
4/8	0.8946
5/8	0.8939
6/8	0.8931
7/8	0.8924
27	0.8917
1/8	0.8910
2/8	0.8903
3/8	0.8896
4/8	0.8889
5/8	0.8882
6/8	0.8875
7/8	0.8868
28	0.8861
1/8	0.8854
2/8	0.8847
3/8	0.8840
4/8	0.8833
5/8	0.8826
6/8	0.8819
7/8	0.8812
29	0.8805
1/8	0.8798
2/8	0.8791
3/8	0.8784
4/8	0.8777
5/8	0.8771
6/8	0.8764
7/8	0.8757
30	0.8750
1/8	0.8743
2/8	0.8736
3/8	0.8730
4/8	0.8723
5/8	0.8716
6/8	0.8709
7/8	0.8702
31	0.8696
1/8	0.8689
2/8	0.8682
3/8	0.8675
4/8	0.8669
5/8	0.8662
6/8	0.8655
7/8	0.8649
32	0.8642
1/8	0.8635
2/8	0.8629
3/8	0.8622
4/8	0.8615
5/8	0.8609
6/8	0.8602
7/8	0.8596
33	0.8589
1/8	0.8582
2/8	0.8576
3/8	0.8569

°Bé.	Sp. gr.
⅛	0.8563
¼	0.8556
⅜	0.8550
½	0.8543
⅝	0.8537
¾	0.8530
⅞	0.8525
34	0.8517
⅛	0.8511
¼	0.8504
⅜	0.8498
½	0.8491
⅝	0.8485
¾	0.8478
⅞	0.8472
35	0.8466
⅛	0.8459
¼	0.8453
⅜	0.8446
½	0.8440
⅝	0.8434
¾	0.8427
⅞	0.8421
36	0.8415
⅛	0.8408
¼	0.8402
⅜	0.8396
½	0.8390
⅝	0.8383
¾	0.8377
⅞	0.8371
37	0.8364
⅛	0.8358
¼	0.8352
⅜	0.8346
½	0.8340
⅝	0.8333
¾	0.8327
⅞	0.8321
38	0.8315
⅛	0.8309
¼	0.8302
⅜	0.8296
½	0.8290
⅝	0.8284
¾	0.8278
⅞	0.8272
39	0.8266
⅛	0.8260
¼	0.8254
⅜	0.8247
½	0.8241
⅝	0.8235
¾	0.8229
⅞	0.8223
40	0.8217
⅛	0.8211
¼	0.8205
⅜	0.8199
½	0.8193
⅝	0.8187
¾	0.8181
⅞	0.8175
41	0.8169
⅛	0.8163
¼	0.8157
⅜	0.8151
½	0.8145
⅝	0.8140
¾	0.8134
⅞	0.8128
42	0.8122
⅛	0.8116
¼	0.8110
⅜	0.8104
½	0.8098
⅝	0.8092
¾	0.8087
⅞	0.8081
43	0.8075
⅛	0.8069
¼	0.8063
⅜	0.8058
½	0.8052
⅝	0.8046
¾	0.8040
⅞	0.8034
44	0.8029
⅛	0.8023
¼	0.8017
⅜	0.8011
½	0.8006
⅝	0.8000
¾	0.7994
⅞	0.7989
45	0.7983
⅛	0.7977
¼	0.7972
⅜	0.7966
½	0.7960
⅝	0.7955
¾	0.7949
⅞	0.7943
46	0.7938
⅛	0.7932
¼	0.7926
⅜	0.7921
½	0.7915
⅝	0.7910
¾	0.7904
⅞	0.7898
47	0.7893
⅛	0.7887
¼	0.7882
⅜	0.7876
½	0.7871
⅝	0.7865
¾	0.7860
⅞	0.7854
48	0.7849
⅛	0.7843
¼	0.7838
⅜	0.7832
½	0.7827
⅝	0.7821
¾	0.7816
⅞	0.7810
49	0.7805
⅛	0.7799
¼	0.7794
⅜	0.7789
½	0.7783
⅝	0.7778
¾	0.7772
⅞	0.7767
50	0.7762
⅛	0.7756
¼	0.7751
⅜	0.7746
½	0.7740
⅝	0.7735
¾	0.7729
⅞	0.7724
51	0.7719
⅛	0.7713
¼	0.7708
⅜	0.7703
½	0.7698
⅝	0.7692
¾	0.7687
⅞	0.7682
52	9.7676
⅛	0.7671
¼	0.7666
⅜	0.7661
½	0.7656
⅝	0.7650
¾	0.7645
⅞	0.7640
53	0.7635
⅛	0.7629
¼	0.7624
⅜	0.7619
½	0.7614
⅝	0.7609
¾	0.7604
⅞	0.7598
54	0.7593
⅛	0.7588
¼	0.7583
⅜	0.7578
½	0.7573
⅝	0.7568
¾	0.7562
⅞	0.7557
55	0.7552
⅛	0.7547
¼	0.7542
⅜	0.7537
½	0.7532
⅝	0.7527
¾	0.7522
⅞	0.7517
56	0.7512
⅛	0.7507
¼	0.7502
⅜	0.7497
½	0.7492

°Bé.	Sp. gr.
57	0.7487
1/8	0.7482
2/8	0.7477
3/8	0.7472
4/8	0.7467
5/8	0.7462
6/8	0.7457
7/8	0.7452
58	0.7447
1/8	0.7442
2/8	0.7437
3/8	0.7432
4/8	0.7427
5/8	0.7422
6/8	0.7417
7/8	0.7412
59	0.7407
1/8	0.7403
2/8	0.7398
3/8	0.7393
4/8	0.7388
5/8	0.7383
6/8	0.7378
7/8	0.7373
60	0.7368
1/8	0.7364
2/8	0.7359
3/8	0.7354
4/8	0.7349
5/8	0.7344
6/8	0.7339
7/8	0.7335
61	0.7330
1/8	0.7325
2/8	0.7320
3/8	0.7315
4/8	0.7311
5/8	0.7306
6/8	0.7301
7/8	0.7296
62	0.7292
1/8	0.7287
2/8	0.7282
3/8	0.7277
4/8	0.7273
5/8	0.7268
6/8	0.7263
7/8	0.7259
63	0.7254
1/8	0.7249
2/8	0.7245
3/8	0.7240
4/8	0.7235
5/8	0.7230
6/8	0.7226
7/8	0.7221
64	0.7216
1/8	0.7212
2/8	0.7207
3/8	0.7203
4/8	0.7198
5/8	0.7193
6/8	0.7189
7/8	0.7184
65	0.7179
1/8	0.7175
2/8	0.7170
3/8	0.7166
4/8	0.7161
5/8	0.7157
6/8	0.7152
7/8	0.7147
66	0.7143
1/8	0.7138
2/8	0.7134
3/8	0.7129
4/8	0.7125
5/8	0.7120
6/8	0.7116
7/8	0.7111
67	0.7107
1/8	0.7102
2/8	0.7098
3/8	0.7093
4/8	0.7089
5/8	0.7084
6/8	0.7080
7/8	0.7075
68	0.7071
1/8	0.7066
2/8	0.7062
3/8	0.7057
4/8	0.7053
5/8	0.7048
6/8	0.7044
7/8	0.7040
69	0.7035
1/8	0.7031
2/8	0.7026
3/8	0.7022
4/8	0.7018
5/8	0.7013
6/8	0.7009
7/8	0.7004
70	0.7000
1/8	0.6996
2/8	0.6991
3/8	0.6987
4/8	0.6983
5/8	0.6978
6/8	0.6974
7/8	0.6970
71	0.6965
1/8	0.6961
2/8	0.6957
3/8	0.6952
4/8	0.6948
5/8	0.6944
6/8	0.6939
7/8	0.6935
72	0.6931
1/8	0.6926
2/8	0.6922
3/8	0.6918
4/8	0.6914
5/8	0.6909
6/8	0.6905
7/8	0.6901
73	0.6897
1/8	0.6892
2/8	0.6888
3/8	0.6884
4/8	0.6880
5/8	0.6875
6/8	0.6871
7/8	0.6867
74	0.6863
1/8	0.6859
2/8	0.6854
3/8	0.6850
4/8	0.6846
5/8	0.6842
6/8	0.6838
7/8	0.6833
75	0.6830
1/8	0.6825
2/8	0.6821
3/8	0.6817
4/8	0.6813
5/8	0.6809
6/8	0.6804
7/8	0.6800
76	0.6796
1/8	0.6792
2/8	0.6788
3/8	0.6784
4/8	0.6780
5/8	0.6776
6/8	0.6771
7/8	0.6767
77	0.6763
1/8	0.6759
2/8	0.6755
3/8	0.6751
4/8	0.6747
5/8	0.6743
6/8	0.6739
7/8	0.6735
78	0.6731
1/8	0.6727
2/8	0.6723
3/8	0.6719
4/8	0.6715
5/8	0.6711
6/8	0.6707
7/8	0.6703
79	0.6699
1/8	0.6695
2/8	0.6691
3/8	0.6687
4/8	0.6683
5/8	0.6679
6/8	0.6675
7/8	0.6671
80	0.6667

THE DETERMINATION OF ARSENIC IN GLYCERINE.

By A. C. Langmuir.

Received October 22, 1898.

THE presence of arsenic in glycerine is probably, by this time, well known to chemists. Several have described its detection qualitatively. Barton,[1] however, was the first to estimate it quantitatively. Barton's method, which was applied on C. P. glycerines only, consists in the charring of five grams of the glycerine with sulphuric and nitric acids, the production of a mirror in the Marsh apparatus, and the comparison of the mirror so obtained with a standard mirror according to Sanger's method.[2]

As it is impossible to draw an accurate comparison if the mirrors weigh over 0.06 milligram, a suitable aliquot part of the solution must be taken, in order to obtain a mirror weighing less than this amount. This requires some experimenting on the part of the analyst, which becomes very tedious if the glycerine be high in arsenic.

These considerations led the author to abandon the method and adopt a modification of Polenske's process,[3] suitable to the case at hand. The method as described by Polenske is accurate with quantities of arsenic up to four to five milligrams. As in glycerine analysis the amount of arsenic in the portion taken rarely exceeds one milligram, the apparatus may be materially simplified.

For analysis we take fifteen to twenty grams of a crude soap lye glycerine and twenty-five to thirty grams of a saponification or C. P. glycerine. With dilute glycerines an amount is taken which would yield the requisite weight upon evaporation. The weighed sample is made up to 100 cc. with hot water and rinsed into a capacious casserole, containing a mixture of 200 cc. of concentrated nitric acid and twelve cc. concentrated sulphuric acid. Cover and heat gently in the hood until the action starts. Remove the flame and wait until the violence of the reaction is over, then boil down slowly over a low flame until dense fumes of sulphuric acid appear. Raise the heat at the end to expel

[1] This Journal, 17, 883.

[2] *Proc. Am. Acad. Sci., 1891*, **26**, 24.

[3] *Chem. Centrbl.* (*1889*), **60**, [2], 58.

the last traces of nitric acid. If the concentration has been a slow one (four to five hours) the organic matter will generally be entirely oxidized. If the acid turns brown, however, from the charring of organic matter it is well to boil for some time longer to complete the oxidation. There is no danger of losing any arsenic by this treatment. Cool and dilute to fifty cc.

About forty grams of coarsely granulated zinc are placed in the generating flask of the Marsh apparatus. A 75 to 100 cc. stop-cock funnel pierces the stopper. The escaping gas is passed through a wash-bottle containing a five per cent. lead nitrate solution to remove any hydrogen sulphide and is dried by passing through a calcium chloride tube. A tube of hard glass about ten inches long and with an inside diameter of ten to twelve mm. is heated near one end and drawn out at that point to a tube with a diameter of one to one and a half mm. This section serves to catch the metallic arsenic deposited. Of the large sections the longer is heated by two Bunsen burners. To prevent sagging it is well to protect this part of the tube with a roll of copper gauze wrapped around it. The shorter section at the end of the tube holds a slip of filter-paper moistened with a saturated solution of mercuric chloride. This serves to detect the presence of any hydrogen arsenide which might pass the burners undecomposed.

After making connections ten cc. of twenty per cent. sulphuric acid is run into the flask. When the air has been entirely displaced rinse the solution to be tested into the stop-cock funnel, light the burners and run the solution, drop by drop, on the zinc at such a rate that not more than two bubbles a second pass the lead nitrate wash-bottle.

If the mercuric chloride paper should at any time show a yellowish tint the solution should be run in more slowly. If the size of the mirror shows that a considerable amount of arsenic is present, it is well to add, at the end, a little stannous chloride dissolved in hydrochloric acid. In any case add a few cubic centimeters of dilute acid after the entire solution has been run in to expel hydrogen arsenide remaining in the flask.

The section carrying the mirror is separated by a file and carefully weighed on an assay gold balance within 0.01 milligram. This can be readily done, as the weight of the tube sel-

dom exceeds 300 milligrams. The arsenic is dissolved by dipping the tube into hot dilute nitric acid, and after washing and drying the weight is taken again, the difference being the weight of the arsenic forming the mirror. The zinc and acids used should not form a perceptible mirror after running the apparatus three quarters of an hour. The following results were obtained:

Arsenic taken. Milligrams.	Arsenic found. Milligrams.
0.20	0.17
0.50	0.45
0.75	0.68

Several C. P. glycerines were found to be free from arsenic. Arsenic was found in a majority of saponification glycerines. These averaged about 0.00018 to 0.00030 per cent. A number of crude soap-lye glycerines gave percentages lying between 0.00064 and 0.01.

A very fair idea of the arsenic contents may be gained by Gutzeit's test, using mercuric chloride instead of silver nitrate. Two cc. of glycerine are run into a five-inch test-tube and diluted with four cc. of water; a piece of granulated zinc is added and sufficient hydrochloric acid to just start the reaction. The tube is then quickly closed by a cork whose lower end is covered with a seven cm. filter-paper. The paper is wrapped around the cork so that it rests smoothly against the lower end. This part is moistened with two drops of a saturated solution of mercuric chloride. The hydrogen escapes through the creases between the paper and the tube. The evolution of hydrogen should be fairly brisk but not too violent.

After standing ten minutes the cork and paper are removed. The latter is spread out and examined. A yellow stain in the shape of a circle with a diameter equal to the end of the cork is formed if arsenic were present. With very impure glycerines the color is brown. The papers carrying the stains may be marked and kept as records for future comparisons. The color is fairly permanent. By comparing the yellow stain produced by the glycerine under examination with a series of standards prepared by running the same test on portions of a solution of arsenic (one milligram in 100 cc.), the per cent. of arsenic can be gauged quite accurately after a little practice. The color is quite distinct with 0.01 milligram of arsenic and is still percepti-

ble with 0.0025 milligram. If the latter amount were present in two cc. glycerine (sp. gr. 1.26) the per cent. of arsenic present would be 0.00010 which would be about the limit of delicacy by this test.

Gutzeit's test using silver nitrate was found to be very unsatisfactory. It is very difficult to form any idea as to the amount of arsenic present from the intensity of the color in this case. The silver nitrate is also so easily affected by impurities in the zinc and acid other than arsenic that any conclusion as to the presence of the latter should be drawn with great caution.

In view of the rapidity, delicacy, and accuracy of Gutzeit's test, using mercuric chloride, it is difficult to understand why the more laborious Marsh test should still hold its own as a qualitative test for arsenic.

LABORATORY OF RICKETTS & BANKS,
NEW YORK.

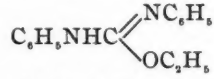
ON THE ISOUREA ETHERS AND OTHER DERIVATIVES OF UREAS.

BY F. B. DAINS.

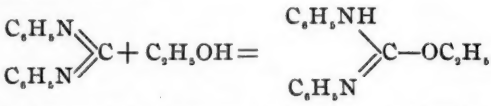
Received December 10, 1898.

THE imido ethers, oxygen ethers of ordinary acid amides or anilides, have since their discovery by Pinner in 1883 been exhaustively investigated in many directions on account of their remarkable reactivity.

In 1894, the first representative of the oxygen ethers of a simple urea, ethyl isocarbanilide



was prepared by Lengfeld and Stieglitz.[1] They found that when carbodiphenylimide was heated to 180° in a sealed tube with absolute alcohol, it added the alcohol quantitatively forming ethylisodiphenylurea.



A little latter they discovered[2] that the ethylisodiphenylurea

1 *Ber. d. chem. Ges.*, 27, 926.
2 *Am. Chem. J.*, 17, 112.

could be prepared without the use of sealed tubes by the action of sodium ethylate upon the hydrogen chloride addition-product of carbodiphenylimide

$$(C_6H_5NH)C(C_6H_5N)Cl + NaOC_2H_5 \rightarrow (C_6H_5NH)C:(NC_6H_5)OC_2H_5 + NaCl.$$

It was finally shown by Stieglitz[1] that the isocarbanilide ethers could be made in a very simple way by the action of sodium ethylate on the alcoholic solution of the carbodiphenylimide. Alcohol is taken up in the cold with great ease under these conditions, while in the absence of sodium ethylate no addition occurs at ordinary temperatures, the diimide polymerizing to $C_3(NC_6H_5)_6$.[2]

These investigations having dealt chiefly with the devising of methods for preparing isourea ethers, at the suggestion, and under the direction, of Dr. Stieglitz, the investigation of the physical constants and particularly of the chemical behavior of this new class of compounds was undertaken by me. The isourea ethers seemed unusually interesting subjects for study, since according to their constitution they are at the same time amidines and imido ethers.

Ethylisodiphenylurea has the amidine grouping, $C:(NC_6H_5)\text{-}(NHC_6H_5)$, and can be called ethoxydiphenylformamidine. It also possesses the characteristic imido ether group, $C:(NC_6H_5)\text{-}(OC_2H_5)$, and hence can be regarded as anilidophenylimidoformic ether. These ethers resemble also the corresponding isothiourea ethers

$$RNHC\begin{matrix}=NR \\ \diagdown SR\end{matrix},$$

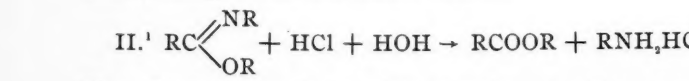
which are more easily prepared and which were consequently discovered,[3] and investigated earlier than the oxygen derivatives.

The most striking results that have been brought out in this investigation are less in the resemblances shown to exist between the above groups of compounds and the isourea ethers, than in the surprising discovery, how deeply the nature of the bodies is modified by the combination of the two typical amidine and imido ether groups in the same molecule.

1 *Ber. d. chem. Ges.*, **28**, 573.
2 *Ibid.*, **27**, 1283; **28**, 1004.
3 *Ibid.*, **12**, 1061; **14**, 1490; **15**, 338.

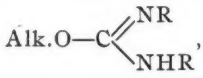
For instance the imido ethers belong to a remarkably active class of compounds,—a fact illustrated by the two following typical reactions. Aniline converts imido ethers easily and smoothly into amidines according to I.

Dilute acids readily decompose the imido ethers even in the cold, forming amines and ethers as in II.



These investigations have proved clearly and without question, the fact that the isodialphylurea ethers give neither one of these typical reactions. The detailed description of their behavior will show that they form a new class of compounds resembling in many features the amidines, imido ethers, and isothiourea ethers, but still differing in a number of fundamental points from these classes of compounds.

Besides the study of the chemical reactions of these isoureas



the methods of preparing them were tested as to their range of applicability, especially where R is an alphyl group.

Finally as a step forward in ascertaining what effect a change in the nature of R had upon the properties and reactions of the urea ethers, R was made carbethoxy ($-COOC_2H_5$). Ethoxydicarbethoxyurea was prepared by a fourth method; namely, from the silver salt of dicarbethoxyurea, a method of synthesis used in the preparation of imido ethers by Tafel and Enoch,[2] Comstock and Wheeler,[3] and others, but which has hitherto failed when applied to ordinary ureas. The study[4] of these new isourea ethers has shown how profoundly a change in the nature of R modifies the chemical nature of the isoureas.

[1] A secondary reaction sometimes occurs due to the fact that the amine formed may react with some unchanged imido ether as in I.

[2] *Ber. d. chem. Ges.*, **23**, 103, 1550.

[3] *Am. Chem. J.*, **18**, 1.

[4] The investigation of the oxygen ethers of aliphatic ureas and carbamide will be continued in this laboratory under the direction of Dr. Stieglitz.

Experimental Part.

I. PREPARATION AND PROPERTIES OF ETHERS OF ISOALPHYLUREAS.

The first ethers synthesized were derivatives of *o*-carboditolylimide, $C_7H_7N=C=NC_7H_7$.

Will and Bielschauski[1] first prepared this body by the decomposition of *o*-tolylimido-*o*-tolylthiomethylcarbamate,

$$C_7H_7N=C\begin{matrix}NHC_7H_7\\SCH_3\end{matrix}.$$

This, when heated, loses mercaptan. They also obtained it by desulphurizing di-*o*-tolylthiourea with mercuric oxide in boiling benzene. It was described by them as an oil soluble in benzene and boiling over 300°.

The diimide used was prepared by this latter method, using carefully purified benzene, pure dry thiourea and yellow mercuric oxide dried at 140°. Lead oxide gives poorer results when used as a desulphurizing agent.

When freshly prepared, *o*-carboditolylimide is a pale yellow oil boiling at the following temperatures:

	Temperature.
15 mm	200°
24 mm	208
28 mm	213
34 mm	223

The index of refraction determined with an Abbe refractometer is 1.624 at the room temperature.

The diimide does not long remain an oil but soon polymerizes, becoming first sticky, then semisolid, and finally a white solid.

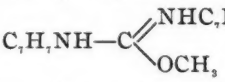
There are certain practical difficulties attending the preparation of the isourea ethers from the diimides, in a pure condition. The carbodiimide must be freshly prepared, since any polymerization that has occurred lessens the yield of the ether, and increases the difficulty of purification. All moisture must be carefully excluded to prevent formation of dialphylurea.

Physically these ethers are oils that must be isolated by fractionation *in vacuo* with this disadvantage; their boiling-points are high and near that of the original diimide. They are

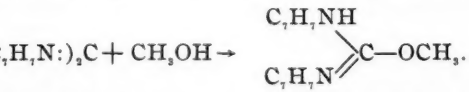
[1] *Ber. d. chem. Ges.*, 15, 1316.

best separated from the diimide by allowing the latter to polymerize by standing, and then extracting with ligroin. This dissolves the urea ethers alone, the solid polymer being entirely insoluble in that solvent.

Methylisodi-o-tolylurea (*o-Tolylimido-o-tolylmethyl Carbamate*),



One molecule of *o*-carboditolylimide was heated for three hours at 180°–190° with a slight excess of absolute methyl alcohol.



The tube opened without pressure and the oily product was allowed to stand in a desiccator for three days. If unchanged carboditolylimide was present it polymerized and became insoluble in ligroin while the urea ether remained soluble. On distilling the ligroin extract, there was obtained besides traces of *o*-carbtoluide and *o*-carboditolylimide, the pure methyl ether boiling at 218° at twenty-nine mm. Analysis:

1. 0.2414 gram substance gave 0.6663 gram carbon dioxide and 0.1598 gram water.

2. 0.4514 gram substance gave 45.3 cc. moist nitrogen at 23° and 747 mm.

	Calculated for $C_{14}H_{18}N_2O$.	Found.
Carbon	75.59	75.27
Hydrogen	7.09	7.36
Nitrogen	11.02	11.17

The yield is nearly quantitative. The same ether was prepared by a second method: the action of sodium methylate in methyl alcohol solution upon the *o*-carboditolylimide. Thirty-five grams of diimide dissolved in two volumes of absolute methyl alcohol were added slowly to a solution of five grams of sodium in seventy-five cc. methyl alcohol, the whole being well cooled in a freezing mixture.

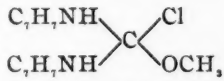
After standing over night a current of carbon dioxide was passed through it. Water was then added, the resulting oil extracted with ether, dried over sodium sulphate, and distilled. Twenty-four grams of pure methyl ether were obtained.

When freshly prepared, methylisodi-*o*-tolylurea is a colorless oil boiling at the following temperatures:

	Temperature.
11 mm	199°
18 mm	206
29 mm	218
32 mm	225

The index of refraction is 1.592 at the room temperature. In a freezing mixture the oil did not solidify but became thick and viscid. However, on standing a number of months a specimen was found to have crystallized in long blunt needles radiating from a common center. It then melted at 48.5° but otherwise exhibited all the characteristics of the oil. Methyliso-*o*-carbtoluide is soluble in ordinary neutral organic solvents, insoluble in water, and soluble in, and more or less rapidly decomposed by, acids such as hydrochloric and acetic.

Action of Hydrogen Chloride (*Methylisodi-o-tolylurea Hydrochloride*,



or

$$(C_7H_7NH)C : (NC_7H_7)OCH_3.HCl.$$

When an ice-cold benzene solution of the methyl ether was saturated with dry hydrogen chloride, there was formed an immediate white crystalline precipitate. This was filtered off with the aid of a pump and dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline. Analysis:

0.1776 gram substance gave 0.0885 gram silver chloride (Carius).

	Calculated for $C_{16}H_{19}N_2OCl$.	Found.
Chlorine	12.20	12.38

Methylisodi-*o*-tolylurea hydrochloride is a white crystalline solid, insoluble in ether, benzene, and ligroin. On exposure to the air it is slowly decomposed by the moisture leaving a residue of *o*-carbtoluide. When heated with water the same decomposition is rapidly effected. In this it differs from the hydrochloride of an ordinary imido ether.

For instance benzimidoethylether hydrochloride,

$$C_6H_5C(NH)OC_2H_5,HCl,$$

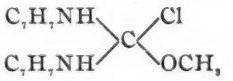
is readily saponified by moisture, the products being ammonium chloride and ethyl benzoate. These reactions will be discussed later in connection with the action of aqueous acids upon the urea ethers. In the absence of moisture methyliso-*o*-carbtoluide hydrochloride is much more stable.

Some of the dry salt was placed in a test-tube connected with an azotometer, the whole apparatus being filled with dry carbon dioxide. At the temperature of the water-bath there was no reaction; it required gentle heating with the free flame to cause any decomposition. Methyl chloride was then split off quantitatively and collected in the azotometer. It was identified by its burning with a green-tinged flame.

$$C_7H_7NHC:(NC_6H_5)OCH_3.HCl \rightarrow CH_3Cl + (C_7H_7NH)_2CO.$$

In a stream of dry hydrogen chloride this stability is much lessened, the loss of alkyl chloride taking place then at a lower temperature. This was shown as follows: dry hydrogen chloride was passed over some of the methyl ether contained in a test-tube connected with an azotometer. At ordinary temperatures there was little decomposition, but on heating to 90° a gas was given off which was not absorbed by the caustic potash, and which burned with a green-tinged flame showing it to be methyl chloride.

The dry hydrogen chloride was first absorbed, but as the temperature increased, methyl chloride split off leaving a white residue. This, after recrystallization from benzene, had the properties and the melting-point (243°) of *o*-carbtoluide. While the hydrochlorides of imido ethers and of urea ethers react differently with moisture, the dry salts decompose with heat in an entirely analogous manner with loss of alkyl chloride.[1] For the constitution of the salts of isocarbanilidoethers, two possibilities present themselves.

I.


II. $C_7H_7NH.C(OCH_3)(NC_7H_7HCl)$ or
$(C_7H_7N:)C(OCH_3)(NC_7H_7H_2Cl)$.

This question will be discussed later. One fact will be

[1] Pinner: *Ber. d. chem. Ges.*, 16, 1654.

brought out here, and that is that although the isocarbanilido ethers are anilidoimido ethers, they are monoacid bases uniting with but one equivalent of hydrogen chloride even in the presence of a large excess of the acid.

This is fully confirmed by the composition of the two chlorplatinates of isocarbanilido ethers which I prepared: those of methyliso-*o*-carbtoluide and of ethylisocarbanilide.

Chlorplatinate of Methyl Iso-o-carbtoluide,

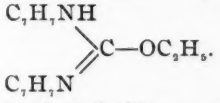
$$[(C_7H_7NH)C(:NC_7H_7)OCH_3]_2H_2PtCl_6.$$

When absolute alcohol solutions of the methyl ether and of chlorplatinic acid were mixed and allowed to stand in a desiccator, the chlorplatinate slowly separated out. It formed hard, red crystals which melted at 155° with decomposition. Analysis:

0.1366 gram substance gave 0.0290 gram platinum.

	Calculated for $C_{32}H_{38}N_4O_2PtCl_6$.	Found.
Platinum	21.25	21.23

Ethylisodi-o-tolylurea (*o-Tolylimido-o-tolyl Ethylcarbamate*),



One molecule of *o*-carboditolylimide was heated with a slight excess of absolute ethyl alcohol at 180°–190° for three hours. The oily contents of the tube were fractionated and a pure product boiling at 215.5° at twenty-four mm. obtained. Analysis:

0.2177 gram substance gave 21.55 cc. moist nitrogen at 25° and 745 mm.

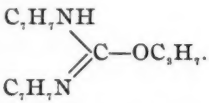
	Calculated for $C_{17}H_{20}N_2O$.	Found.
Nitrogen	10.45	10.80

Ethylisodi-*o*-tolylurea is a colorless oil which does not solidify at —5°. Its index of refraction is 1.606 at the room temperature. Heated to 80° in a stream of dry hydrogen chloride, ethyl chloride is split off, leaving a solid residue of *o*-carbtoluide. This was recrystallized from benzene and identified by its properties and melting-point.

In the preparation of urea ethers by the method given too high temperatures must be avoided. This was shown in the following experiment. A mixture of diimide and absolute alcohol was heated at 215°–220° for several hours and then for

a short time at 250°. The tube opened with much pressure and a gas escaped that burned with a luminous flame. This was probably ethylene. The contents of the tube consisted of an oil and a white solid which proved to be *o*-carbtoluide. The oil yielded on distillation *o*-ditolylurea, *o*-carboditolylimide and only a small amount of impure ethylisocarbtoluide. This was identified by the formation of ethyl chloride which burned with a green-tinged flame. As will be seen later the above substances are the decomposition products of the ethyl ether at high temperatures.

n-Propylisodi-o-tolylurea,



Twenty grams of the carbodiimide and ten grams propyl alcohol were heated at 180°–200° for six hours. The tube opened without pressure and the oil on distillation gave the pure propyl ether. The yield is nearly quantitative. Analysis:

0.4246 gram substance gave 39.5 cc. moist nitrogen at 22° and 744 mm. pressure.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	10.36

n-Propylisodi-*o*-tolylurea is a colorless oil, soluble in ordinary organic solvents. It does not solidify in a freezing-mixture. The boiling-point is 212°–214° at fourteen mm.

Dry hydrogen chloride was passed into a solution of the propyl ether in benzene and ligroin. The slight white precipitate first formed readily dissolved as the current of gas was continued. An oil which was soluble in benzene but insoluble in ligroin separated out on standing. This, when heated, gave propyl chloride and *o*-carbtoluide, showing that it contained the hydrochloride. An effort was made to isolate this as follows:

The oil obtained by the action of hydrogen chloride was washed with a mixture of benzene and ligroin (b. p. 40°–60°), and the excess of solvent evaporated in a current of dry air in a vacuum desiccator over stick potash, sulphuric acid, and vaseline. A clear, yellow oil resulted. Analysis:

0.5610 gram substance heated with lime required 15.8 cc. tenth-normal silver nitrate (Volhard).

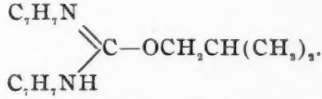
0.5166 gram substance gave 32.8 cc. moist nitrogen at 17.5° and 740 mm.

	Calculated for $C_{18}H_{23}N_2OCl$.	Found.
Chlorine	11.13	9.98
Nitrogen	8.79	7.18

The low results are doubtless due to traces of solvent obstinately retained by the oil. That it is mainly the hydrochloride is shown by the analysis and the decomposition products, propyl chloride and *o*-carbtoluide.

The oil solidified on standing in a desiccator but, as analysis indicated, this was caused by the gradual formation of *o*-ditolylurea.

Isobutylisodi-o-tolylurea,



Sixteen grams of *o*-carboditolylimide were heated for six hours at 180°–210° with a slight excess of isobutyl alcohol. The contents of the tube yielded on distillation a clear colorless oil, boiling at 218° at 18 mm. Analysis showed that it was the isobutyl ether.

0.3250 gram substance gave 27.7 cc. moist nitrogen at 24° and 755 mm.

	Calculated for $C_{19}H_{24}N_2O$.	Found.
Nitrogen	9.46	9.54

Isoamylisodi-o-tolylurea,

Forty-one grams diimide were dissolved in amyl alcohol (b. p. 130°–131°), and then poured into a well-cooled solution of sodium amylate (one molecule). The mixture became slightly warm. After standing over night carbon dioxide was passed into the solution, which was then washed with water, dried with sodium sulphate, and distilled. The pure amyl ether was obtained as a colorless oil boiling at 206° at 10 mm. Its index of refraction is 1.572 at the room temperature. The yield is about equal to the diimide taken. Analysis:

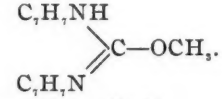
0.3586 gram substance gave 29.2 cc. moist nitrogen at 18° and 747 mm.

	Calculated for $C_{20}H_{16}N_2O$.	Found.
Nitrogen	9.03	9.28

p-Carboditolylimide, $C_7H_7N{=}C{=}NC_7H_7$.—This was prepared in the hope that the higher melting para-derivatives would give solid ethers instead of oils—a wish that was not realized. The diimide was first described by Will[1] as a body melting above 60° and boiling above 300° without decomposition. The substance was made in the usual manner by the desulphurization of the thiourea. In general *p*-carboditolylimide is less reactive than the carbodiphenyl or *o*-ditolylimides. The para body and its ethers distil about 20° higher than the corresponding *o*-tolyl compounds and tend to form viscid gums difficult to purify.

Pure *p*-carboditolylimide is a pale yellow oil boiling at 221°–223° at 20 mm.

Methyl Isodi-p-tolylurea,



Twenty-three grams of the diimide were heated with methyl alcohol for seven hours at 180°–200°. In distilling the product a considerable portion came over below 200°. From the higher fraction, there was isolated the pure methyl ether boiling at 220° at fifteen mm. Analysis :

0.4580 gram substance gave 43.8 cc. moist nitrogen at 16° and 739 mm.

	Calculated for $C_{16}H_{18}N_2O$.	Found.
Nitrogen	11.02	10.89

The methyl ether forms a clear, thick oil. In a stream of dry hydrogen chloride it is somewhat more stable than the methyl iso-*o*-carbtoluide, since methyl chloride only splits off above 100°. From the fraction below 200° an oil was obtained which boiled at 86°–88° at fourteen mm. and which turned red on standing. This gave the following results on analysis :

0.4148 gram substance gave 0.3202 gram water and 1.1510 grams carbon dioxide.

[1] *Ber. d. chem. Ges.*, **14**, 1488.

0.3108 gram substance gave 27.5 cc. moist nitrogen at 16.5° and 736 mm.

	Calculated for $C_7H_7NH\diagdown C(OCH_3)_2\diagup C_7H_7NH$	$C_7H_7NH\diagdown C(=N\,C_7H_7)-OCH_3$	Found.
Carbon	71.33	75.70	75.59
Hydrogen	7.69	8.58	8.66
Nitrogen	9.79	11.02	10.24

It was thought that the compound might be the dimethyl ether, but the theory was not borne out by the analytical figures. At the same time, while the results agree fairly closely with those required for an isomeric ether, the great difference in boiling-point, 140° at fourteen mm., would seem to preclude this idea. Owing to lack of material, further examination of this oil was deferred for the present.

Methyl isodi-*p*-tolylurea was also prepared by another method, the action of sodium methylate on the monohydrochloride of *p*-carboditolylimide.

$$C_7H_7N=C(C_7H_7N)-\boxed{Cl+Na}OC_2H_5.$$

One molecule of hydrogen chloride in ether solution was added to *p*-carboditolylimide also dissolved in ether. No effort was made to isolate the hydrochloride, but sodium methylate in methyl alcohol was added directly to the solution. After filtering off the sodium chloride and some *p*-carbtoluide, the ether was evaporated and the residue extracted with ligroin. This, on distillation, gave a poor yield of methyl isodi-*p*-tolylurea.

0.4488 gram substance gave 46 cc. moist nitrogen at 25° and 755 mm.

	Calculated for $C_{16}H_{18}N_2O$.	Found.
Nitrogen	10.02	11.42

n-Propyl Isodi-p-tolylurea,

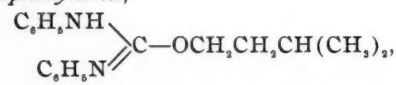
$$C_7H_7NH\diagdown C(=N\,C_7H_7)-O-CH_2CH_2CH_3.$$

On heating propyl alcohol and *p*-carboditolylimide at 180° for four hours, the propyl ether which boils at 221° at sixteen mm. was formed. It is a thick viscid oil at ordinary temperatures. Analysis:

0.4380 gram substance gave 36.8 cc. moist nitrogen at 18° and 760 mm.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	9.75

Isoamylisodiphenylurea,

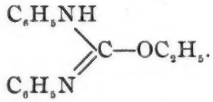


was prepared by the action of sodium amylate upon carbodiphenylimide in amyl alcohol (b. p. 130°–131°) solution. The procedure was the same as with the isoamyliso-*o*-carbtoluide. It is a colorless oil boiling at 210° at fifteen mm. At the room temperature the index of refraction is 1.594. Analysis:

0.2280 gram substance gave 19.5 cc. moist nitrogen at 16° and 749 mm.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	9.86

Ethylisocarbanilide,



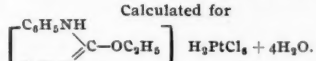
This was prepared by Lengfeld and Stieglitz,[1] who described it as a limpid stable oil boiling at 200° at 20 mm. They also isolated the hydrochloride of the ethyl ether, a white solid melting at 60°–80° with decomposition. Its action toward chlorplatinic acid is interesting.

It has been shown previously that methyl isodi-*o*-tolylurea with chlorplatinic acid, gives in absolute alcohol solution, an anhydrous salt in which the urea ether acts as a monacid base. On the other hand ethyl isocarbanilide forms, in absolute alcohol solution, no crystallizable derivative of the ethyl ether, but, in dilute alcoholic solutions, gives very readily a chlorplatinate containing water of crystallization. To a water solution of chlorplatinic acid was added a dilute alcoholic solution of ethyl isocarbanilide. On evaporation, the platinum salt separated out in the form of hard, red crystals which melted at 113° with decomposition. Analysis:

[1] *Ber. d. chem. Ges.*, **27**, 926.

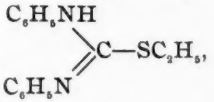
I. 0.1630 gram substance gave 0.0330 gram platinum.

II. 0.3750 gram substance gave 0.0762 gram platinum.



	Calculated for	Found.	
		I.	II.
Platinum	20.28	20.25	20.32

The same salt is formed in both dilute and concentrated alcoholic solutions. The corresponding thioether,



gives a platinum salt containing two molecules of water of crystallization.[1] In the preparation of the urea ethers described above, three methods have been used.

1. The addition of alcohol at high temperatures to the carbodiimide.

2. The action of sodium ethylate upon an alcoholic solution of the carbodiimide.

3. The action of sodium ethylate upon the monochloride of the carbodiimide.

Of these methods, the first gives good results and is of universal applicability. It requires, however, the use of sealed tubes. The second method gives equally good yields; it does not require high temperatures, and by it larger amounts of the urea ether can be prepared at one time. It necessitates, however, the use of a large excess of the alcohol. The third method offers no advantage over the other two. It involves the intermediate formation of the monohydrochloride, a compound very sensitive toward moisture. It requires also a greater number of operations with a corresponding decrease in yield.

The urea ethers thus far prepared are, with one exception, oils; methyl iso-*o*-carbtoluide alone on long standing solidified to a crystalline mass. On the other hand ethyl isocarbanilide, prepared in 1894 by Dr. Stieglitz, is still an unchanged oil.

The urea ethers dissolve readily in neutral organic solvents and are insoluble in water. All acid solvents react with them. While they cannot be distilled at ordinary pressure without

[1] Rathke: *Ber. d. chem. Ges.*, 14, 1776.

decomposition, they can uniformly be fractionated *in vacuo* without change. The index of refraction is in all cases observed less than that of the original diimide. This can serve as a test of the purity of the ether since the presence of the diimide causes an increase in the index of refraction.

INDEX OF REFRACTION.

Carbodi-*o*-tolylimide	1.624
Methyl iso-*o*-carbtoluide	1.592
Ethyl iso-*o*-carbtoluide	1.606
Amyl iso-*o*-carbtoluide	1.572
Ethyl isocarbanilide[1]	1.6028
Amyl isocarbanilide	1.594

The experiments just described show that the formation of a urea ether by the addition of an alcohol to the carbodiimide is a general reaction of which all aromatic carbodiimides are capable; these take up the various primary and secondary fatty alcohols without difficulty. In every case the alcohol was added smoothly according to

$$\text{I. } RN{=}C{=}NR + R'OH \rightarrow \begin{matrix} RNH \\ \diagdown \\ RN \end{matrix}\!\!>\!C{-}OR',$$

and with none of the many alcohols tested did the carbodiimide simply cause the splitting off of water according to

$$\text{II. } (RN{:})_2C + C_nH_{2n+1}OH \rightarrow (RNH)_2CO + C_nH_{2n},$$

forming a carbanilide and an unsaturated hydrocarbon.

Such compounds were indeed obtained by heating carbodi-*o*-tolylimide and ethyl alcohol much higher than the temperatures necessary for forming the urea ethers,[2] but, as will be shown later, the urea ethers themselves give, on heating the same products, a carbanilide and an olefine hydrocarbon.

$$\text{III. } RNHC(:NC)OC_nH_{2n+1} \rightarrow (RNH)_2CO + C_nH_{2n}.$$

These facts prove that either urea ethers are formed as intermediate products when carbodiphenylimide and an alcohol react according to II, or that the absorption of alcohol by the unsaturated carbodiphenylimide molecule to form a urea ether takes

[1] J. Stieglitz: *Ber. d. chem. Ges.*, 28, 574.

[2] Page 143.

place much below the temperature at which an alcohol breaks down into water and an olefine.

$$\text{IV. } C_nH_{2n+1}OH \rightleftarrows C_nH_{2n} + H_2O.$$

Such a reaction would become one-sided from the absorption of water by the carbodiphenylimide according to

$$\text{V. } H_2O + C(:NC_6H_5)_2 \rightarrow (C_6H_5NH)_2CO,$$

and give the reaction products of II.

Either of these conclusions—and there is no other third possible view of the action of carbodiphenylimide on the alcohols—is sufficient to throw clear light on some of the next reactions that were studied, and in the interpretation of the results of such study reference will be made to the conclusions just established.

II. ISOACYLALPHYLUREAS; ACTION OF DRY ACIDS ON CARBODIIMIDES.

The ease with which carbodiphenylimide absorbs alcohols suggested the attempt to prepare by the same kind of reaction,—using acids—a most interesting group of bodies, the acid salts of carbodiphenylimide or isoacylcarbanilides according to

$$\text{VI. } (C_6H_5N:)_2C + HOAcyl \rightarrow (C_6H_5NH)C(:NC_6H_5)OAcyl.$$

As such salt like isoacyl derivatives the addition products of carbodiphenylimide and hydrogen chloride must be considered, and these were investigated by me somewhat further than they had been previously. Weith,[1] by passing dry hydrogen chloride into a benzene solution of carbodiphenylimide, prepared the monochloride which he analyzed and to which he assigned the formula $(C_6H_5N)_2C.HCl$.

Further investigation by Lengfeld and Stieglitz[2] showed the conditions for preparing the monochloride, and proved that a dichloride $(C_6H_5N)_2 2HCl$ and a sesquichloride $[(C_6H_5N)_2C]_2 3HCl$ are much more readily precipitated even if much less than one molecular equivalent of hydrogen chloride is used. These are white crystalline compounds that can be isolated and analyzed. Such salts were also obtained by me from the carboditolylimides and carboallylphenylimide.

Work done in this laboratory by Mr. H. N. McCoy,[3] under the

[1] *Ber. d. chem. Ges.*, 7, 11.
[2] *Am. Chem. J.*, 17, 107.
[3] *Ibid.*, 21, 111; *Ber. d. chem. Ges.*, 30, 1090, 1685.

direction of Professor Stieglitz, has fully confirmed the conclusions of Stieglitz and Lengfeld that the monochloride has the constitution of an isoacylcarbanilide

$$(C_6H_5N:)_2C+HCl \rightarrow \begin{matrix} C_6H_5NH \\ \diagdown \\ \quad\quad C \\ \diagup\!\!\diagup \\ C_6H_5N \end{matrix} \!\!>\!C-Cl,$$

and still it has the appearance of a salt.[1] I have been able to confirm the salt-like character of such a monochloride[2]—whatever its constitution—by preparing chlorplatinates of analogous composition, which in appearance, composition, and behavior resemble the chlorplatinates of any organic base.

Action of Hydrochloric Acid and of Hydrochlorplatinic Acid on the Carbodialphylimides; Monochlorplatinate of Carbodiphenylimide, $[(C_6H_5N)_2C]_2H_2PtCl_6$.—When an absolute alcohol solution of carbodiphenylimide is treated with chlorplatinic acid also dissolved in absolute alcohol, a darkening in color occurs, but there is no precipitate unless the solution is very concentrated. In that case a dark, red salt separates. This melts at 155°–165° and contains, as shown by analysis, an excess of platinum over that required by the monochlorplatinate. (26.00 per cent. instead of 24.44). If ether be added to the clear alcoholic solution, a yellow platinum salt corresponding to the monochlorplatinate is obtained. This was washed with ether, dried at 90°, and analyzed. Analysis:

0.1118 gram substance gave 0.0270 gram platinum.

	Calculated for $[(C_6H_5N:)_2]_2H_2PtCl_6$.	Found.
Platinum	24.44	24.15

The chlorplatinate[3] is soluble in alcohol, insoluble in ether, and not readily decomposed by water. It begins to decompose at 143° and melts completely to a reddish oil at 150°. In several cases a salt containing one or two per cent. more of platinum with a higher melting-point (155°–165°) was obtained, but in no instance did this correspond to the dichlorplatinate,

$$[(C_6H_5N)_2C].H_2PtCl_6 (Pt=32.19).$$

[1] The dichloride must therefore have the constitution $(C_6H_5NH)_2CCl_2$ or $Cl.C(C_6H_5NH):(C_6H_5N)HCl$. The former is more likely and is being further investigated in this laboratory.

[2] *Am. Chem. J.*, 21, 101.

[3] It can also be prepared by mixing ethereal solutions of the diimide and chlorplatinic acid. It is then precipitated out immediately.

The Dichlorplatinate of Carbodiphenylimide, $[(C_6H_5N:)_2C]\text{-}H_2PtCl_6$.—The latter body, the chlorplatinate, corresponding to the dichloride, was not formed by the action of an excess of chlorplatinic acid upon the diimide. This was in decided contrast to the action of hydrogen chloride upon the diimide. Thus carbodiphenylimide monochloride was isolated with considerable difficulty by Lengfeld and Stieglitz,[1] who prepared it by passing hydrogen chloride into a solution of the carbodiimide; but there was a constant tendency for the reaction to go farther and form the sesqui- and dichlorides.

The dichlorplatinate of carbodiphenylimide was, however, obtained in the following unexpected manner: An effort was made to prepare an anhydrous chlorplatinate of ethyl isocarbanilide using absolute alcohol solutions; with dilute alcohol a hydrated salt is obtained.[2] While this end was not realized a still more interesting compound, the platinum salt of carbodiphenylimide dichloride was obtained.

When absolute alcoholic solutions of ethyl isodiphenyl urea and chlorplatinic acid were mixed, there gradually separated out, in small quantity, reddish-brown needles which did not melt at 250°. For analysis these crystals were washed with alcohol and ether and dried at 80°. Analysis:

I. 0.0802 gram substance gave 0.0258 gram platinum.

II. 0.1325 gram substance gave 0.0430 gram platinum.

	Calculated for $[(C_6H_5N)_2C]H_2PtCl_6$.	Found. I.	II.
Platinum	32.30	32.17	32.45

The results agree with the composition of the platinum salt of carbodiphenylimide dichloride. So far as the analysis is concerned it agrees also with the composition of aniline chlorplatinate (Pt=32.80), but against this latter view are the following facts:

a. The salt does not resemble at all in appearance aniline chlorplatinate.

b. The salt after treatment with caustic soda did not respond to the bleaching-powder test for aniline.

c. Aniline could only be formed from urea ether hydrochloride by saponification as follows:

[1] *Am. Chem. J.*, 17, 110.

[2] Page 148.

$$\begin{matrix} C_6H_5NH \\ \diagdown \\ \quad C{=}OC_2H_5 + HOH \rightarrow \\ \diagup \\ C_6H_5N \end{matrix}$$

$$C_6H_5NH_2.HCl + C_6H_5NHCOOC_2H_5.$$

The residue was examined but no trace of phenyl urethane could be detected.

Such a chlorplatinate of carbodiphenylimide could, however, be formed as follows:

In the absolute alcohol solution slight dissociation might occur into alcohol and carbodiphenylimide. This latter then unites with the chlorplatinic acid which was present in very great excess, forming the dichlorplantinate of carbodiphenylimide.

o-Carboditolylimide Dichloride, $C_7H_7N{:}C(NHC_7H_7)Cl.HCl$.—It had been previously noted by Will and Bielschauski[1] that a solution of *o*-carboditolylimide with hydrogen chloride gave a white precipitate, but the product formed was not analyzed. Dry hydrochloric acid gas was passed into *o*-carboditolylimide dissolved in twenty times its weight of dry benzene.

The diimide must be especially purified by several distillations, otherwise gummy impurities are found. The stream of gas was continued as long as any absorption took place, the solution meanwhile being kept cool. A heavy white precipitate formed at first which soon redissolved, and on standing there was deposited from the clear solution hard granular crystals. These were dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline for thirty-six hours. Analysis:

0.1898 gram heated with lime required 13.37 cc. tenth-normal silver nitrate (Volhard).

	Calculated for $C_{15}H_{16}N_2Cl_2$.	Found.
Chlorine	24.06	24.96

o-Carboditolylimide is a white solid, insoluble in ligroin and benzene, but soluble in chloroform. It melts with decomposition at 235°–237°. Moisture decomposes it giving *o*-carbtoluide and hydrogen chloride.

$$(C_7H_7NH)C{:}(NC_7H_7)Cl.HCl + H_2O \rightarrow 2HCl + (C_7H_7NH)_2CO.$$

o-Carboditolylimide Monochlorplatinate, $[(C_7H_7N)_2C]_2H_2PtCl_6$.—Ethereal solutions of the diimide and of chlorplatinic acid were

[1] *Ber. d. chem. Ges.*, 15, 1316.

mixed; a yellow platinum salt was immediately precipitated which was washed with ether dried at 100°, and analyzed. Analysis:

0.1850 gram substance gave 0.0420 gram platinum.

	Calculated for $[(C_7H_7N)_2C]_2H_2PtCl_6$.	Found.
Platinum	22.84	22.70

The salt begins to decompose at 146°–148°; at about 155° it melts completely. The same salt was obtained even with a large excess of chlorplatinic acid.

p-Carboditolylimide Monochlorplatinate.—This body which was prepared from ethereal solutions of chlorplatinic acid and *p*-carboditolylimide as in the previous cases, is a yellow salt that begins to decompose at 148° and melts completely between 155° and 160°.

0.1828 gram substance gave 0.0410 gram platinum. Analysis:

	Calculated for $[(C_7H_7N)_2C]H_2PtCl_6$.	Found.
Platinum	22.84	22.43

Sesquichloride of p-Carboditolylimide.—When a concentrated benzene solution of pure-*p*-carboditolylimide was saturated with dry hydrochloric acid gas, the solution which became warm was filled with a thick, heavy, white precipitate of the hydrochloride. Analysis showed that this was a mixture of chlorides and not a definite chemical compound.

Two determinations of different preparations gave respectively 17.80 and 17.33 per cent. chlorine. The monochloride contains 13.73 per cent. chlorine, the sesquichloride 19.21 per cent., and the dichloride 24.06 per cent.

With a five per cent. benzene solution better results were obtained. The precipitate first formed nearly all dissolved on continuing the stream of gas, while the filtered solution on standing a few hours in a vacuum desiccator deposited a large crop of crystals. These melted at 126°–127° forming an oily gum. Analysis:

I. 0.2418 gram substance heated with lime required 13.1 cc. tenth-normal silver nitrate (Volhard).

II. 0.1840 gram substance required 10.1 cc. tenth-normal silver nitrate.

	Calculated for $(C_{13}H_{14}N_2)_23HCl$.	Found. I.	II.
Chlorine	19.22	19.20	19.46

Sesquichloride of Carboallylphenylimide.—Analogous results were obtained with carboallylphenylimide. The experiments with hydrogen chloride will be given here, but the discussion of the diimide reserved until later.

Dry hydrochloric acid gas was passed into a benzene solution of carboallylphenylimide. A precipitate formed, which, as the current of gas was continued, almost entirely dissolved. The filtered solution, on standing, deposited crystals. These were dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline, and analyzed. Analysis:

0.1778 gram substance heated with lime required 12.23 cc. tenth-normal silver nitrate.

	Calculated for $\left(\begin{matrix}C_6H_5N \\ C_6H_5N\end{matrix}\!\!>\!C\right)_2 3HCl$.	Found.
Chlorine	25.00	24.39

The monochloride requires 18.23 per cent. chlorine and the dichloride 30.73 per cent. The product obtained is evidently a sesquichloride. Lengfeld and Stieglitz,[1] who first prepared a body of this class—carbodiphenylimide sesquichloride, say this regarding it: "The substance may be a mixture of monochloride and dichloride in nearly molecular quantities. It was very frequently obtained and seems to have more or less characteristic properties by which it can be identified."

But the fact that three different carbodiimides give compounds of this class argues strongly in favor of a definite chemical composition and against their being merely mechanical mixtures.

These sesquichlorides, $[(RN:)_2C].\ 3HCl$, show an interesting analogy to the isocyanides which also form hydrochlorides of this type, $(RNC)_23HCl$.[2]

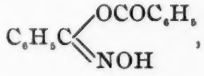
The Action of Organic Acids upon the Carbodialphylimides, as has been stated previously, was studied with the object of obtaining isoacylureas of the general type

$$\begin{matrix}RNH \\ \diagdown \\ \quad C{=}O\ \text{Acyl}, \\ \diagup \\ RN\end{matrix}$$

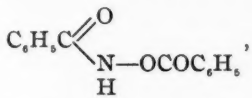
[1] *Am. Chem. J.*, 17, 110.

[2] Gautier: *Ann. chim. phys.*, 17, 223; Nef: *Ann. Chem.* (Liebig), 270, 277; *Ber. d. chem Ges.*, 31, 1770.

corresponding to the alkyl ethers and the chlorides just described. This seemed an especially inviting subject for investigation since the instances of true isoacyl derivatives of acid amides are exceedingly rare, and their behavior very interesting. Such an acyl derivative was prepared by Werner[1] in the form of dibenzhydroximic acid,

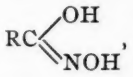


by the action of silver benzoate on benzhydroximic acid chloride. He found it a peculiarly reactive body since, even on standing, it suffers molecular change going over into its isomer,

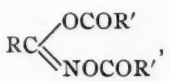


the benzoyl ester of benzhydroxamic acid.

If both hydrogen atoms of a hydroxamic acid,



are replaced by acyl groups,



such molecular change is prevented and more stable bodies are obtained. These, however, with alkali lose with great ease the acyl group joined to carbon.[2] These facts would indicate the reactivity and unstability of the acyl isomers, could they be isolated.

The organic acids, such as acetic and formic, do react very readily with the carbodiimides even at low temperatures, and although the desired acyl isoureas were not isolated, a very interesting reaction was discovered, in which there is hardly any doubt that the acyl isoureas figure as intermediate products.

Ten grams of *o*-carboditolylimide were treated with an excess

[1] *Ber. d. chem. Ges.*, 27, 2198.

[2] Jones: *Am. Chem. J.*, 20, 19 and 32.

of glacial acetic acid. The mixture became decidedly warm and soon solidified, while a distinct odor of acetic anhydride manifested itself.

The solid residue, after purification with ligroin and benzene, was dried on a clay plate. Its properties, melting-point (243°), and analysis showed that it was *o*-carbtoluide.

Analysis:

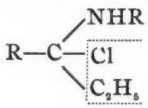
0.2418 gram substance gave 25.2 cc. moist nitrogen at 20° and 747 mm.

	Calculated for $C_{15}H_{16}N_2O$.	Found.
Nitrogen	11.66	11.77

In a second experiment ten grams of *o*-carboditolylimide (one mol.) were mixed with five grams of glacial acetic acid (two molecules) in a distilling bulb. When the reaction was completed and the product distilled from an air-bath, the main portion of the distillate came over between 130°–138°. It was fairly constant at 137°. This liquid had the odor and boiling-point of acetic anhydride and reacted directly with aniline, giving acetanilide. The residue in the flask proved to be *o*-carbtoluide.

The low temperature at which the reaction occurs is shown by the following experiment: A ligroin solution of acetic acid was added slowly to a ligroin solution of the diimide cooled to —18°. At —15° the formation of *o*-carbtoluide was very slow; at 0° the reaction went somewhat faster and at ordinary temperatures was soon over.

In view (1) of the facts discussed previously[1] that alcohols are added to the carbodiimides much below the temperature at which they suffer loss of water; (2) the very ready formation, isolation, and analysis of the dichlorides of carbodiphenylimide and *o*-carboditolylimide; (3) the decomposition of hydrochlorides of imido ethers according to



into acid amides and alkyl chlorides, a decomposition that

[1] Page 150.

takes place the more readily the more acid the molecule;[1] (4) the fact that the reaction takes place at —10°, a temperature at which glacial acetic acid does not lose water nor carbodiimide take it up, the formation of acetic anhydride by the action of acetic acid upon *o*-carboditolylimide cannot possibly be considered as due to direct splitting off of water from the acid. The facts mentioned show rather that the results must be due to a series of reactions; as with hydrogen chloride, there must be addition of the acetic acid to the double bond of the *o*-carboditolylimide forming a very unstable diacetate, which even at temperatures below zero decomposes, forming acetic anhydride and *o*-carbtoluide,

$$\begin{matrix} C_7H_7N \\ C_7H_7N \end{matrix}\!\!\gg C + 2CH_3COOH \rightarrow$$

$$\begin{matrix} C_7H_7NH \\ C_7H_7NH \end{matrix}\!\!\gg C\!\!\begin{matrix} O\,COCH_3 \\ OCOCH_3 \end{matrix} \rightarrow (C_7H_7NH)_2CO + (CH_3CO)_2O,$$

corresponding to the loss of an alkyl chloride and the formation of an acid amide above.[2]

Action of Formic Acid.—Since this reaction, at so low a temperature (—15°) resulted in the formation of an acid anhydride, it was tried with formic acid whose anhydride $(CHO)_2O$ is as yet unknown.

Again, it was found that instead of such an anhydride carbon monoxide was formed.[3] *o*-Carboditolylimide diluted with an equal volume of benzene, was put in a test-tube fitted with a small dropping-funnel and connected with an azotometer. The air in the apparatus was displaced with dry carbon dioxide and the diimide solution cooled to —10°.

Pure formic acid was allowed to flow into the diimide slowly, when a gradual evolution of gas, unabsorbed by the caustic potash, occurred. On removing the freezing-mixture the evolution

[1] Thus the chloride of ethylphenylimidochlorformate, Cl—C(:MR)OC_2H_5, decomposes at —15° (Lengfeld and Stieglitz, *Am. Chem. J.*, 16, 73) and the hydrochloride of ethoxydicarbethoxyurea,

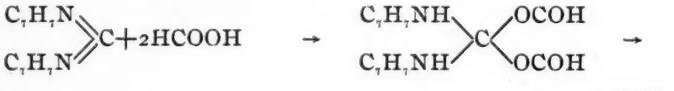
$$\begin{matrix} C(OC_2H_5)NHCOOR \\ \| \\ NCOOR \end{matrix},$$

loses ethyl chloride at 0° (page 188).

[2] Page 158.

[3] Nef: *Ann. Chem.* (Liebig), 270, 278.

of gas became more rapid and the benzene solution was filled with a white precipitate. This was found to be *o*-carbtoluide while the gas in the azotometer burned with a blue flame and proved to be carbon monoxide. As with the acetate, there must be formation of a diformate which, even at —15°, separates into *o*-carbtoluide and formic anhydride. This latter compound, which has never been isolated, breaks down immediately into carbon monoxide and water.



$$(C_7H_7NH)_2CO + O\begin{matrix}COH\\COH\end{matrix}.$$

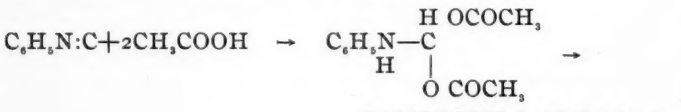
$$(COH)_2O \rightarrow 2CO + H_2O.$$

The grouping RN=C= is common to both the carbodiimides, RN=C=NR, and the isonitrils, RN=C=, and the experiments just given bring out two interesting analogies between them.

These are (1) the formation of sesquichlorides, $(RNC)_23HCl$, and (2) the formation of acid anhydrides with acetic and formic acids.

Gautier,[1] in his researches upon the isonitrils, discovered that methyl and ethyl isocyanide give with acetic acid the anhydride.

Nef[2] more recently has shown that phenyl isocyanide reacts in like manner with acetic and formic acids at —10° giving the acid anhydride or carbon monoxide and formanilide. The facts enumerated above show that the result in these cases is also probably due to a like sequence of reactions.

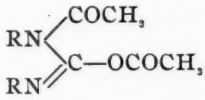


One molecule of acid adds to the bivalent carbon; the other to the double bond between carbon and nitrogen.

Since the isoacyl derivatives were found to be so unstable

[1] Gautier: *Ann. chim. phys.*, [4], 17, 223, 241.
[2] Nef: *Ann. Chem.* (Liebig), 270, 277, 278.

splitting off acid anhydrides even at —10°, the action of acetic anhydride upon the diimide was tried as it was possible that an acetyl isoacetate like



would be more stable. Molecular proportions of acetic anhydride and *o*-carboditolylimide were mixed. Since no reaction occurred at ordinary temperature, the mixture was then heated at 160° for several hours in a sealed tube. The tube opened with much pressure due to carbon dioxide. The product of the reaction was an oil which did not solidify on standing.

It was doubtless more or less pure *o*-diacettoluide, which is itself an oil. No effort was made to isolate it but it was treated directly with dilute caustic soda and the resulting *o*-acettoluide purified and identified.

I. $(RN:)_2C+2(CH_3CO)_2O \rightarrow CO_2+2RN(COCH_3)_2$.

II. $RN(COCH_3)_2+NaOH \rightarrow CH_3COONa+RNHCOCH_3$.

It is possible that addition-products are formed analogous to those mentioned before but they are hardly of sufficient importance to be discussed here.

III. CARBOALLYLPHENYLIMIDE.

Only one attempt has as yet been made to prepare an isourea ether of an aliphatic amine. For this purpose carboallylphenylimide was chosen. This seemed especially suitable, since, according to Bizio,[1] allylphenylthiourea gives a carbodiimide, and the ethers of such a body containing both an aliphatic and an alphyl group should show a gradation in properties between the fatty and aromatic isourea ethers.

While the efforts to obtain the isourea ethers in a pure condition were unsuccessful in this case, the results of the experiments shed interesting light upon carboallylphenylimide and correct some errors that have crept into the literature of the allylphenyl derivatives. Zinin[2] first tried the desulphurization of allylphenylthiourea. He used lead oxyhydrate in alcoholic

[1] Bizio: *Jsb. d. Chem.*, *1861*, 497.
[2] Zinin: *Ibid.*, *1862*, 628.

solution and obtained a compound which was described as crystallizing in long silky needles; no melting-point was given.

Bizio[1] repeated this work and isolated a body which melted at 105°. To this he ascribed the formula $C_{10}H_{10}N_2$ and the constitution

$$\begin{matrix} C_3H_5N \\ \quad\quad > CN. \\ C_6H_5 \end{matrix}$$

In Beilstein's "Handbuch" and in Watts' "Dictionary of Chemistry" this same compound is called phenylallylcyanamide or carboallylphenylimide and to it is given the normal carbodiimide constitution,

$$C_6H_5N{=}C{=}NC_3H_5.$$

That this compound is carboallylphenylimide is impossible both from its method of preparation and its properties.

The thiourea was desulphurized in dilute alcohol solution and the resulting product was soluble in acetic acid without change; both reactions should give an oxygen urea and this was found to be no exception to the rule. The allylphenylthiourea was desulphurized in the usual manner with mercuric oxide in absolute benzene solution. After evaporating off the benzene a mobile oil was left, but on distillation it gave no pure products. At ten mm. pressure fractions were collected between (I) 150°–165°; (II) 165°–170°; (III) 190°–200°. This latter is the boiling-point of carbodiphenylimide.

Fraction I was analyzed and gave figures agreeing with carboallylphenylimide.

Analysis:

0.2502 gram substance gave 38.5 cc. moist nitrogen at 18° and 749 mm.

	Calculated for $C_{10}H_{10}N_2$.	Found.
Nitrogen	17.72	17.58

It, however, is not quite pure, since whenever any attempt was made to redistil it, some decomposition occurred with the formation of a high boiling residue.

In the hope that the corresponding urea ethers might be more stable, the undistilled carboallylphenylimide was treated in abso-

[1] *Jsb. d. Chem*, *1861*, 497; *J. prakt. Chem.*, 86, 292.

lute alcohol solution with sodium ethylate. The urea ether was isolated in the usual manner.

When the urea ether was distilled fractions were obtained that gave ethyl chloride with hydrochloric acid showing the presence of a urea ether, but no compound of a definite boiling-point could be obtained. These results indicated the impossibility of obtaining a pure carbodiimide or urea ether by distillation; hence the attempt in this direction was abandoned.

The mobile oil just described as being obtained when allylphenylthiourea ether is desulphurized with mercuric oxide in benzene solution, is very different in appearance and properties from the carboallylphenylimide described in literature as a solid (m. p. 105°) and obtained by desulphurization in dilute alcohol solution. It seemed now of interest to ascertain whether the undistilled oil is the carbodiimide and also to find out what Bizio's product that melted at 105° really was. Any analytical determinations of the composition of this oil would be of little value since it cannot be obtained entirely pure, but that it is nearly pure carboallylphenylimide is proved by its reactions and the products derived from them.

As has been shown[1] distillation breaks it up into mixtures of carboallylphenylimide, carbodiallylimide, and carbodiphenylimide. It reacts, like other carbodiimides, with alcohol and sodium alcoholate giving impure urea ethers.[2] With dry hydrogen chloride it forms a definite sesquichloride,

$$\left(\begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}\!\!>\!\!C\right)_2 3HCl.^3$$

It has just been shown[4] that the carbodiimides react smoothly with formic acid with the evolution of carbon monoxide and the formation of the corresponding urea.

The oily diimide was treated with formic acid. Abundant evolution of a gas occurred; this burned with a blue flame and proved to be carbon monoxide. The residue was purified by crystallization from water. A small amount of diphenylurea melting at 235° was obtained, but the main product was a solid

[1] Page 162.
[2] Page 162.
[3] Page 156.
[4] Page 159.

melting at 113°. Later experiments showed that this solid was pure allylphenylurea formed according to

$$C_3H_5N : C : NC_6H_5 + 2HCOOH \rightarrow \begin{matrix} C_3H_5NH \\ C_6H_5NH \end{matrix} > CO + 2CO + H_2O.$$

These reactions, together with its method of preparation, conclusively show that the oil really is a carbodiimide, and its almost quantitative conversion into allylphenylurea proves that, undistilled, it is nearly pure carboallylphenylimide.[1]

Bizio prepared his so-called carboallylphenylimide melting at 105° by desulphurizing the thiourea in alcoholic solution. This work was repeated to see if like results could be obtained. The semisolid product of the reaction was purified by crystallization from dilute alcohol and hot water. In one experiment a small quantity of diphenylurea was isolated, but the main product is the same solid, melting at 113°, that was obtained by the interaction of formic acid on carboallylphenylimide, and which, as will presently be shown, is allylphenylurea. The change in melting-point from 105° to 113° is due to a complete purification of the compound.

Allylphenylurea, $C_3H_5NHCONHC_6H_5$.—As the melting-point 113° does not correspond to the melting-points given in literature, either for allylphenylurea, 97°, nor for diallylurea,[2] 100°, these two ureas were prepared synthetically. Diallylurea, which was made by the desulphurization of allyl mustard oil in alcoholic solution differs widely in appearance and properties (m. p. 100°) from the above body (m. p. 113°). Allylphenyl-

[1] An effort was made to ascertain the composition of this oil by changing it into a guanidin derivative. Equal molecules of aniline and allylphenylthiourea were boiled with mercuric oxide in dilute alcoholic solution. This should give allyldiphenyl guanidine. The gummy mass left after distilling off the alcohol was repeatedly extracted with boiling dilute hydrochloric acid and the hydrochloride obtained subjected to fractional crystallization. The fractions all gave the same base, which was curiously enough triphenyl guanidine. This was proved by its melting-point, 148°, and the analysis of the platinum salt.

I. 0.5217 gram substance gave 0.1032 gram platinum.

II. 0.2700 gram substance gave 0.0525 gram platinum.

	Calculated for $C_{38}H_{36}N_6PtCl_6$.	Found. I.	II.
Platinum	19.82	19.78	19.44

No other definite compound could be isolated.

[2] Maly : *Z.* (2), **5**, 258.

[3] Will : *Ann. Chem.* (Liebig), **52**, 25.

urea was made from allylamine and phenyl isocyanate.[1] The method suggested by Gabriel and Eschenbach[2] was found to give good results in the preparation of allylamine.

Ethereal solutions of allylamine and phenyl isocyanate reacted readily with the formation of an oil which, after treatment with water, solidified. The allylphenylurea was purified by crystallization from the same solvent. It then formed fine needles, melting at 113°, soluble in hot water and ordinary organic solvents.

Analysis:

0.2060 gram substance gave 29 cc. moist nitrogen at 24° and 753 mm.

	Calculated for $C_6H_5NH\rangle CO.$ C_3H_5NH	Found.
Nitrogen.....	15.91	15.73

This synthetic allylphenylurea is identical in appearance, properties, and melting-point with the compounds obtained by desulphurizing allylphenylthiourea in alcoholic solution, and by treating carboallylphenylimide with formic acid. Mixtures of these with the synthetic preparation melted constantly at 113°, thus proving their identity.

The compound prepared by Bizio[3] and described in literature as carboallylphenylimide is therefore not that, but the corresponding urea; and the melting-point of pure allylphenylurea is 113°, and not 97° as given by Maly.[4]

CHEMICAL BEHAVIOR OF THE ISOUREA ETHERS.

Besides the experiments upon the preparation of alphyl and acyl isourea ethers and of isoallylphenylureas, attention was paid particularly to a thorough investigation of the action of

[1] The phenyl isocyanate was prepared as follows: A mixture of five grams phenyl urethane and six grams phosphorus pentachloride was heated at 70° in a distilling-bulb fitted with an air-condenser until no further evolution of gas took place. The phosphorus oxychloride was then distilled over, at the temperature of the water-bath, in a current of dry hydrogen chloride. After driving off the excess of hydrochloric acid gas with a stream of dry air, the residue was distilled. The yield of phenyl isocyanate was nearly quantitative, and the reaction seems to be a most convenient one for rapidly preparing small quantities of phenyl isocyanate. This method is one suggested by Lengfeld and Stieglitz (*Am. Chem. J.*, 15, 71) and later used by Folin for preparing isocyanates (*Am. Chem. J.*, 19, 336).

[2] *Ber. d. chem. Ges.*, 30, 1124.

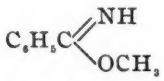
[3] *Jsb. d. Chem.*, *1861*, 497.

[4] *Z.* (2), 5, 258.

various reagents upon the isourea ethers, especially reagents that are typical in their action upon the amidines, imido ethers, and thio urea ethers.

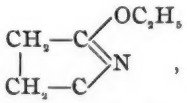
Action of Water.—Ethyl isodiphenylurea is insoluble in water and can remain in contact with it for long periods without formation of carbanilide, or other noticeable change.

No decomposition followed when a mixture of the ether with a large excess of water was evaporated almost to dryness. This is in marked contrast to the imido ethers. Thus benzimidomethyl ether,[1]



on exposure to the air or in water solution, after a month's standing, changes to benzamide.

Comstock and Wheeler[2] have also shown that oxygen ethyl succinimide,



with water regenerates succinimide with great ease, while traces of moisture entirely prevent its preparation.

The Action of Dilute Hydrochloric Acid.—It has been shown in an earlier part of this paper that the isourea ethers unite easily and smoothly with dry hydrogen chloride to form definite crystalline hydrochlorides, which in the absence of moisture, are stable at ordinary temperatures. When heated, the dry salts split quantitatively into alkyl chloride and dialphyl urea. In the main, the same general reaction was found to occur in aqueous solutions. Methyl isodi-*o*-tolylurea was dissolved in very dilute hydrochloric acid with the aid of a few drops of alcohol, and the solution allowed to stand at the ordinary temperature. In a few hours crystals began to appear which gradually increased in amount, until the solution was examined a month later.

1 Wheeler: *Am. Chem. J.*, 17, 398.
2 *Ibid.* 13, 7.

The crystalline deposit proved to be *o*-carbtoluide (m. p. 243°).[1] The clear solution, on warming with a few drops of hydrochloric acid, gave a slight precipitate of *o*-carbtoluide, showing that a little unchanged ether was still present after remaining a month in the acid solution. When the latter solution was made alkaline with ammonia a slight white deposit was obtained, which corresponded to the properties and melting-point of tri-*o*-tolylguanidine.

Ethylisodiphenylurea was dissolved in one per cent. hydrochloric acid under like conditions. A slow deposition of carbanilide began, which was not complete after a month's standing. On warming the solution still more carbanilide was thrown down, showing that the solution still contained unchanged urea ether. The clear filtrate gave, with ammonium hydroxide, only traces of triphenylguanidine (m. p. 143°). At 100° this same decomposition is fully completed in a few hours. Methylisodi-*o*-tolylurea was heated for four hours with dilute hydrochloric acid in a Victor Meyer water-bath. The tube opened with slight pressure, due to methyl chloride which burned with a green flame. The other products were, as before, *o*-ditolylurea, and traces of tritolylguanidine. The action of hydrogen chloride in aqueous solution upon ethyl isocarbanilide yields, therefore, carbanilide and ethyl chloride, according to

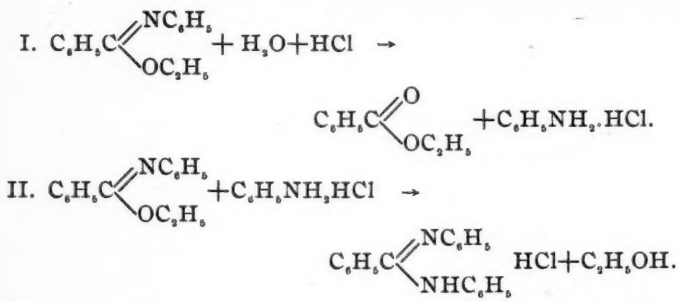
$$RNH.C(NR)OC_2H_5 + HCl \rightarrow RNHCONHR + C_2H_5Cl.$$

Many experiments were made in the effort to trace out the course of this exceedingly important reaction so that it could be positively ascertained whether the reaction followed the lines of the decomposition of ordinary imido ethers, and if it did not, to ascertain wherein the difference lay.

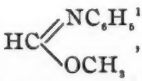
When phenylbenzimidoethyl ether is allowed to stand in hydrochloric acid solution,[2] or is warmed with the same, the reaction which occurs proceeds in two stages: There is first, saponification into aniline hydrochloride and ethyl benzoate; secondly, the aniline hydrochloride reacts with unchanged imido ether to form diphenylbenzamidine and alcohol.

[1] The identity of these compounds was proved by taking the melting-point of a mixture of the suspected body with one of known constitution.

[2] *Ann. Chem.* (Liebig), 265, 138.

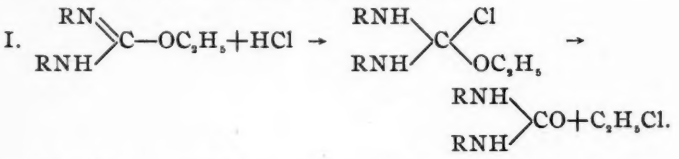


Toward dilute acid, or even water alone, methyl isoformanilide,

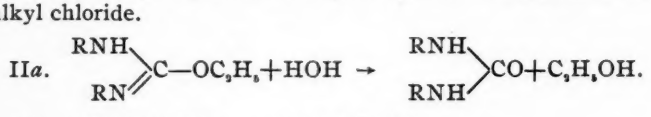


is peculiarly sensitive. The first products are methyl formate and aniline hydrochloride, but this latter immediately reacts with unchanged imido ether to give much diphenylformamidine. The primary products, then, of the decomposition of ordinary imido ethers, are esters and amine hydrochlorides, while a secondary reaction yields amidine hydrochlorides and alcohol. No ethyl chloride is formed in dilute aqueous solution.

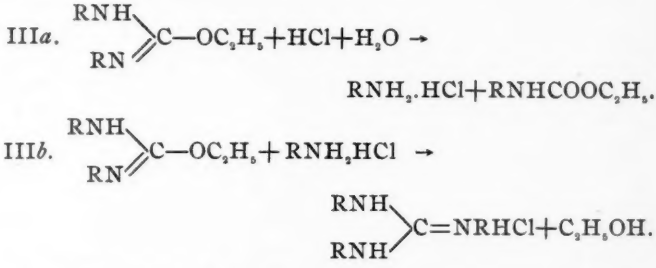
When the isourea ethers are decomposed in aqueous solution into ethyl chloride and carbanilide, several possibilities present themselves for the mechanism of the reaction.



This is the same reaction that occurs when the dry hydrochloride is heated, a quantitative splitting into dialphylurea and alkyl chloride.



Carbanilide and alcohol are first formed by saponification, while the ethyl chloride is due to a reaction between the alcohol and hydrochloric acid.



III*a*. $\mathrm{RNH}\diagdown\!\!\diagup\mathrm{C{-}OC_2H_5}+\mathrm{HCl}+\mathrm{H_2O}\rightarrow$ RN

$\mathrm{RNH_2.HCl}+\mathrm{RNHCOOC_2H_5}.$

III*b*. $\mathrm{RNH}\diagdown\!\!\diagup\mathrm{C{-}OC_2H_5}+\mathrm{RNH_2HCl}\rightarrow$ RN

$\mathrm{RNH}\diagdown\mathrm{C{=}NRHCl}+\mathrm{C_2H_5OH}.$ $\mathrm{RNH}\diagup$

III*c*. $\mathrm{RNHCOOC_2H_5}+\mathrm{RNH_2HCl}\rightarrow$

$(\mathrm{RNH})_2\mathrm{CO}+\mathrm{C_2H_5OH}+\mathrm{HCl}.$

$\mathrm{C_2H_5OH}+\mathrm{HCl}\rightarrow\mathrm{C_2H_5Cl}+\mathrm{H_2O}.$

This involves (*a*) the formation of aniline hydrochloride and phenyl urethane. These two compounds might, in turn, give carbanilide and alcohol as a primary reaction, while a small amount of the aniline hydrochloride reacts with unchanged isourea ether to form triphenylguanidine.

It will be noticed that III*a* and III*b* follow exactly the lines of decomposition of ordinary imido ethers.

When ethyl isodiphenylurea and one per cent. hydrochloric acid are heated at 100° for eight hours, the tubes open with slight pressure, due to ethyl chloride. The main product is carbanilide; traces of triphenylguanidine are also present.

A test for alcohol with benzoyl chloride and caustic soda gave negative results. This shows that the reaction cannot proceed according to II. Since ethyl alcohol and aqueous hydrochloric acid do not give ethyl chloride, alcohol should be in the solution, but the above test proved its absence.

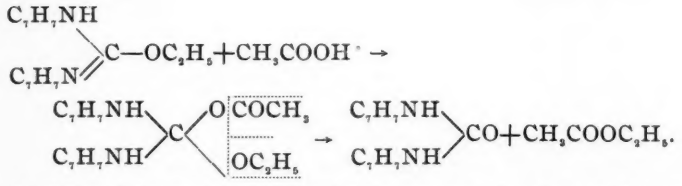
Bearing upon equation III are the following data: In one experiment the contents of the tube, after treatment with alkali, gave a few drops of oil which the bleaching-powder test showed to be aniline (III*a*). Between aniline and the urea ethers there is no reaction. (See below.)

When, however, ethyl isocarbanilide is heated with a dilute

aqueous solution of aniline hydrochloride at 100°, traces of triphenylguanidine are obtained (III*b*). But when phenyl urethane and aniline hydrochloride were heated for eight hours in a sealed tube at 100°, the tube opened without pressure; no carbanilide and no ethyl chloride were obtained. The phenyl urethane was recovered unchanged; this disproves the possibility of III*c*. Hence the formation of carbanilide and ethyl chloride, the main products of the action of dilute aqueous hydrochloric acid on ethyl isocarbanilide, cannot proceed according to III. I alone accounts fully for the formation of these compounds. Equation I, therefore, positively represents the true action of aqueous hydrochloric acid on urea ethers in its principal phase. The formation of the by-product, triphenyl guanidine, takes place, as just shown, by the secondary reactions, III*a* and III*b*. These reactions bring out the radical point of difference between the imido ethers and the urea ethers. With the former, the reactions corresponding to III*a* and III*b* are the exclusive ones, or predominate.[1]

With the urea ethers, I has become the most prominent, while III*a* and III*b* are almost entirely absent.[2]

Action of Glacial Acetic Acid.—When a slight excess of glacial acetic acid was added to ethylisodi-*o*-tolylurea, the formation of a white solid and of ethyl acetate, recognized by its odor, was observed. The reaction was completed by heating in an oil-bath at 130° for a short time. When examined, the solid residue proved to be pure *o*-carbtoluide. The course of the reaction is as follows:



Addition of the acetic acid doubtless occurs, forming an inter-

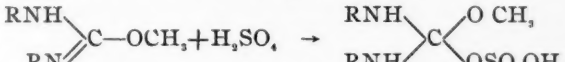
[1] A reaction according to I does not seem to be recorded in the literature of the ordinary imido ethers, but it is thought that a careful investigation will show that it takes place to a very small extent.

[2] These facts seem to shed valuable light on the constitution and behavior of the hydrochlorides of imido ethers and urea ethers. Their bearing on this subject will be discussed by Dr. Stieglitz in a paper on the subject in the *Am. Chem. J.*, **21**, 101.

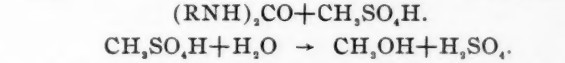
mediate acetate, which is too unstable to be isolated. This addition-product begins to decompose at ordinary temperatures, giving acetic ether and *o*-carbtoluide, a reaction analogous in every way to that with hydrochloric acid. Amylisodi-*o*-tolylurea and acetic acid slowly react at ordinary temperatures, and on warming to the boiling-point of the latter, decomposition is soon effected. Two products were obtained, *o*-ditolylurea, identified by its melting-point and properties, and amyl acetate, recognized by its odor.

Action of Dilute Sulphuric Acid.—Dilute sulphuric acid acts upon the isourea ethers less readily than hydrochloric acid. In the cold the complete decomposition is very slow. On heating methylisodi-*o*-tolylurea with five per cent. sulphuric acid in a sealed tube at 100°–110° for four hours, complete saponification followed. The tube opened without pressure. Much *o*-carbtoluide had crystallized out, and the clear solution gave no test for urea ether on heating with dilute hydrochloric acid.

Ammonium hydroxide gave a very slight precipitate—possibly of tritolylguanidine—but the amount was not sufficient for identification. The presence of methyl alcohol was shown by the benzoyl chloride test. The reaction evidently follows the same lines as that with dilute hydrochloric acid.

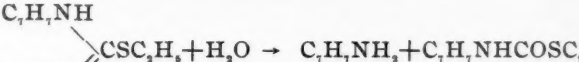


$$(RNH)_2CO+CH_3SO_4H.$$



The relation of the decomposition here to that of the imido ethers is the same as in the preceding cases.

The action of strong sulphuric acid was tried in order to compare the relative behavior of oxygen and thiourea ethers. Will and Bielschauski[1] found that when ethylthiodi-*o*-tolyl urea was heated with twenty per cent. sulphuric acid at 160°–170° for three hours, incomplete saponification followed, with the formation of *o*-toluidine and monothio-*o*-tolyl urethane.



[1] *Ber. d. chem. Ges.*, **13**, 1317.

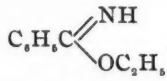
Ethyl isocarbanilide was heated under like conditions. The tube opened with pressure due to carbon dioxide. The contents of the tube, which formed a clear, dark-brown solution, were shaken out with ether. This yielded nothing, showing the absence of phenyl urethane. This acid solution, when neutralized, gave an oil which the bleaching-powder test proved to be aniline. Complete saponification according to

$$(C_6H_5N{:})C(NHC_6H_5)OC_2H_5+H_2SO_4+2H_2O \rightarrow (C_6H_5NH_3)_2SO_4+C_2H_5OH+CO_2$$

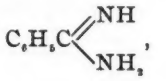
evidently takes place.

Carbanilide, the first saponification product according to p. 171, I, I found, is completely saponified by twenty per cent. sulphuric acid at 150°–160°, in the course of three hours. Phenyl urethane, the first saponification product to be expected according to the behavior of the thiourea ethers (p. 171, II) is, according to my observations, much more slowly decomposed under the same conditions, considerable urethane being recovered. There is no doubt, therefore, that even toward twenty per cent. sulphuric acid, at 160°, urea ethers first lose alcohol and not aniline, by saponification, in marked contrast to the thiourea ethers and ordinary imido ethers.

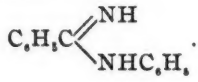
Action of Ammonia and Aniline.—Reference has been made[1] to what is doubtless one of the most characteristic reactions of the imido ethers; that is, the remarkable ease with which they react with ammonia or substituted amines in the cold or on warming slightly to form amidines. Thus, benzimido ether,



reacts readily and smoothly with ammonia to form benzamidine,

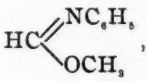


and with aniline to form phenylbenzamidine,

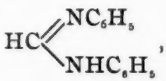


[1] Page 138.

Methyl isoformanilide,



with aniline or aniline hydrochloride gives a quantitative yield of diphenylformamidine,



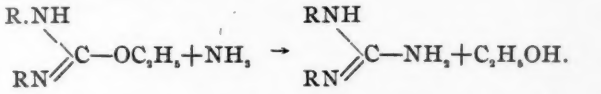
while the oxygen ethers of succinimide react with aniline with evolution of heat to form an amidine derivative.[1]

Judging then from analogy alone, the isourea ethers which contain this same grouping should react readily to form substituted guanidines. The results of the experiments directly contradicted this expectation, and showed the surprising stability of the isourea ethers toward basic reagents.

A solution of ethylisodiphenyl urea in alcoholic ammonia was heated at 130°–140° for several hours. The tube, which opened without pressure, contained an oil which was soluble in hydrochloric acid, and did not respond to any of the tests for aniline. On warming the acid solution, carbanilide and ethyl chloride were formed, showing that the oil consisted of unchanged urea ether. No trace of triphenylguanidine could be found in the acid filtrate.

When the ammoniacal solution was heated to 190°–200°, partial reaction occurred. Traces of diphenylguanidine were isolated, but most of the ether was unchanged.

On heating methylisodi-*o*-tolyl urea with alcoholic ammonia at 200° for three hours, a very incomplete conversion into di-*o*-tolylguanidine (m. p. 179°) took place.



It has been previously shown[2] that ethylisodiphenyl urea and aqueous aniline hydrochloride at 100° give carbanilide and traces, but only *slight* traces, of triphenylguanidine. An effort

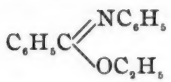
[1] Comstock and Wheeler: *Am. Chem. J.*, 13, 10.

[2] Page 169.

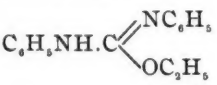
was made to prepare triphenylguanidine directly from the two substances. Molecular proportions of aniline and urea ether were heated in an oil-bath at 140°–150° for several hours. The oily product gave a test for aniline, and on warming with dilute hydrochloric acid, in which it dissolved, carbanilide was deposited, showing the presence of unchanged urea ether.

The acid filtrate contained no trace of triphenylguanidine. As there was no reaction at the temperature employed, the mixture was heated at 290°–300° for five hours. The tube, which opened with pressure, was filled with combustible gases. It contained aniline, traces of urea ether, and a few crystals of carbanilide but no triphenylguanidine. The explanation of this will be seen in the action of heat upon the urea ether alone.

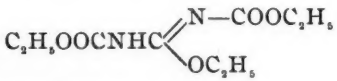
These experiments with ammonia and aniline show clearly the remarkable stability of the urea ethers, as compared with the imido ethers. The explanation for this must lie in the fact that the addition of an anilido group, C_6H_5NH, to the imido ether complex has made the molecule more positive. If more negative groups are introduced into a urea ether, as is the case with the ethoxy ether of dicarbethoxy urea, ammonia again reacts easily and smoothly with the formation of a guanidine.



reacts easily with ammonia and aniline.



reacts with ammonia with great difficulty, and not at all with aniline.



reacts easily with ammonia.

This same effect of increasing the negative nature of the molecule is seen in the behavior of the thiourea ethers. Here a much greater activity is noticed. Thus ethylthiodiphenyl urea reacts at 120° with alcoholic ammonia to form mercaptan and

diphenylguanidine[1] while boiling with aniline is sufficient to convert methylthioditolyl urea into phenylditolylguanidine and methylsulphhydrate.[2]

Action of Heat upon the Urea Ethers.—The results of the last experiment with aniline and urea ether led to trying the effect of heat alone.

Ethylisodiphenyl urea was heated for five hours at 295°–300°, and a gas, ethylene, escaped, which burned with a luminous flame. The residue, which was a semisolid mass mixed with crystals, consisted of carbanilide and polymerized carbodiphenylimide. The formation of polymerized carbodiphenylimide in this reaction would indicate that the decomposition of ethyl isocarbanilide is not directly into ethylene and carbanilide, which gives phenyl isocyanate, but no carbodiphenylimide. It is, then, far more likely that at this high temperature the isocarbanilides are decomposed back into carbodiphenylimide and alcohol, the reaction by which they are formed being reversed;[3]

$$(C_6H_5N:)_2C+C_2H_5OH \rightleftarrows \begin{matrix} C_6H_5NH \\ \diagdown \\ C_6H_5N \end{matrix} \!\!=\!\! C\!-\!OC_2H_5,$$

and the alcohol breaking down partly into ethylene and water, the latter combines with the carbodiimide to form carbanilide.[4]

Action of Potassium Hydroxide.—A solution of methyliso-*o*-carbtoluide in strong alcoholic potash is not decomposed by long standing or even by boiling.[5] The recovered oil responded to the tests for the urea ethers. Some of the urea ether, dissolved in alcoholic potash, was heated in a sealed tube at 160° for three hours. The tube opened without pressure. When the alcoholic solution was acidified with hydrochloric acid there was an evolution of carbon dioxide; no unchanged urea ether was found. The solution contained, however, an oil soluble in the acid.

[1] Rathke: *Ber. d. chem. Ges.*, 14, 1776.

[2] *Ibid.*, 15, 1309.

[3] Page 140.

[4] Ethyl thiocarbanilide (or toluide) breaks down in like manner on heating into ethylmercaptan and carbodiphenylimide.

[5] Methyl thiocarbanilide breaks down into carbanilide and mercaptan when boiled with alcoholic potash.

$$\begin{matrix} RNH \\ \diagdown \\ RN \end{matrix} \!\!=\!\! C\!-\!SCH_3 + H_2O \rightarrow (RNH)_2CO + CH_3SH.$$

Will: *Ber. d. chem. Ges.*, 14, 1489.

This, with benzoyl chloride, gave *o*-benztoluide (m. p. 143°) and was, therefore, *o*-toluidine. Methylisodi-*o*-tolyl urea shows the same stability toward boiling ten per cent. caustic soda. No saponification follows.[1] When heated with the aqueous alkali for three hours at 160° the decomposition was complete. The carbon dioxide was absorbed by caustic soda and the *o*-toluidine identified by changing into *o*-benztoluide. The clear solution contained methyl alcohol. This was shown by the benzoyl chloride test. The reaction can doubtless be represented as follows:

$$a.\quad \begin{matrix}RNH\\RN\end{matrix}\!\!>\!C\!-\!OCH_3+H_2O \rightarrow \begin{matrix}RNH\\RNH\end{matrix}\!\!>\!CO+CH_3OH$$

$$b.\quad \begin{matrix}RNH\\RNH\end{matrix}\!\!>\!CO+H_2O \rightarrow 2RNH_2+CO_2.$$

Experiment showed that a dialphyl urea, such as carbanilide, was readily and completely saponified at 160° by ten per cent. aqueous or alcoholic potash.

These experiments have brought out incidentally the relative stability toward acids and alkalies of the oxygen and thiourea ethers. By hydrochloric, sulphuric, and acetic acids,[2] the oxygen ethers are gradually decomposed in the cold, but readily when heated, while the opposite is true of the thiourea ethers. Thus, methyl thiocarbanilide can be boiled with strong hydrochloric acid without change; decomposition[3] into aniline and mercaptan is only effected by heating with concentrated acid at 150°. With basic reagents the oxygen ethers show a much greater stability.

Previous experiments have shown their inertness[4] toward ammonia, aniline, and caustic alkalies. On the other hand, the same reagents react with relative ease with the thiourea ethers.[5]

Action of Hydrogen Sulphide.—Many of the experiments thus far described have borne directly upon the relation between the urea ethers, the imido ethers, and the thiourea ethers. It must

[1] Ethyl isocarbanilide heated at 120°–130° for six hours, under like conditions, gave mainly unchanged urea ether, only traces of aniline, and no carbanilide.

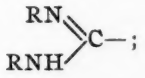
[2] Pages 166, 171, 170.

[3] Weith: *Ber. d. chem. Ges.*, 14, 1490.

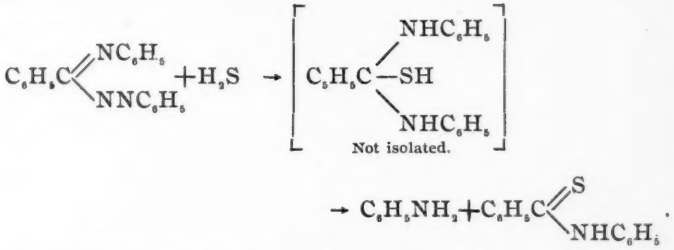
[4] Pages 172 and 175.

[5] *Ber. d. chem. Ges.*, 14, 1489 and 1490.

not be forgotten that the urea ethers contain also the amidine grouping



and hence could show some of the typical reactions of the amidines. Bernthsen[1] has found that there are two reagents, hydrogen sulphide and carbon disulphide, that react in an especially characteristic manner with this class of compounds. Thus, if α-benzenyldiphenylamidine is heated at 160°–165° in a stream of dry hydrogen sulphide, there is a quantitative splitting into aniline and thiobenzanilide.



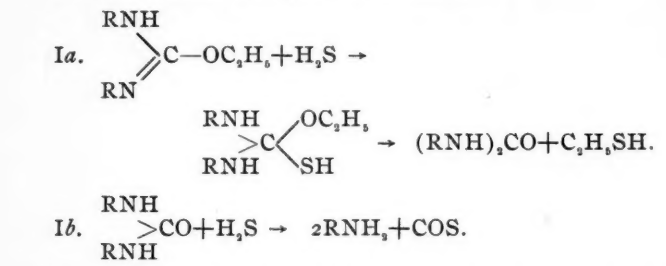
The carbon disulphide reaction, which is somewhat similar, will be discussed later.

Dry hydrogen sulphide was passed over ethylisodiphenyl urea in a distilling bulb immersed in an oil-bath. This was connected with another distilling bulb, which served as a receiver, while the gaseous products of the reaction were led over alcoholic ammonia for the purpose of absorbing any carbon disulphide that might be formed. At 130°–140° there was no reaction, the urea ether remaining unchanged. When the temperature was raised to 180°–190° slow decomposition began. A few drops of oil distilled over in the receiver. This was soluble in hydrochloric acid, and responded to the bleaching-powder test for aniline, and with benzoyl chloride gave benzanilide. A slight residue of carbanilide was left in the distilling bulb. When the solution of alcoholic ammonia was evaporated to dryness and the residue taken up with water, it gave, with ferric chloride, a test for ammonium thiocyanate, showing that car-

[1] *Ann. Chem.* (Liebig), **192**, 32.

bon disulphide had been absorbed. Mercaptan, C_2H_5SH, was recognized among the gaseous products by its odor. Any reaction, then, must take into account the formation of these compounds: carbanilide, aniline, carbon disulphide, and mercaptan.

Three possibilities are open to consideration:



Ia. $RNH{>}C{=}RN - OC_2H_5 + H_2S \rightarrow$

$RNH{>}C(RNH)(OC_2H_5)(SH) \rightarrow (RNH)_2CO + C_2H_5SH.$

Ib. $RNH{>}CO + H_2S \rightarrow 2RNH_2 + COS.$

The hydrogen sulphide, which is a weak acid, acts in this case like hydrogen chloride, the unstable addition-product breaking down.

IIa. $RNH{>}C(RNH)(OC_2H_5)(SH) \rightarrow (RNH)_2CS + C_2H_5OH.$

IIb. $(RNH)_2CS + H_2S \rightarrow 2RNH_2 + CS_2.$

Here ethyl alcohol is lost, instead of mercaptan, from the addition-product, giving thiocarbanilide.

IIIa. $RNH(RNH)C(OC_2H_5)(SH) \rightarrow RNHCSOC_2H_5 + RNH_2$

IIIc. $RNHCSOC_2H_5 + H_2S \rightarrow RNH_2 + CS_2 + C_2H_5OH.$

The intermediate phenylthiourethane is saponified in much the same way as with dilute acids. It will be noticed that III is the only one in which the normal decomposition of amidines is followed out.

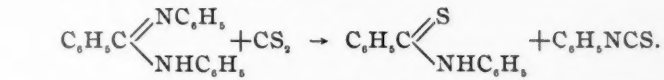
The formation of mercaptan and carbanilide proves that the reaction certainly proceeds, to some extent, according to I*a*. That this could also account for some of the aniline was shown by a special experiment.

Carbanilide at 190° was found to be *very slowly* attacked by

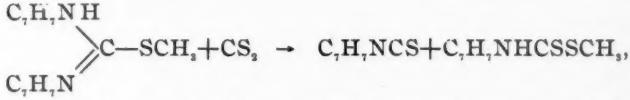
hydrogen sulphide with the formation of aniline (I*b*). The exceeding slowness of this reaction, however, as compared with the action of hydrogen sulphide upon the urea ethers, makes it certain that reaction II or III, or both, must occur.

No further experimental evidence was obtained on this point; but the general fact that the urea ethers lose much more readily the alkyl group giving carbanilides[1] than an aniline group giving urea ethers, would be in favor of II.

Action of Carbon Disulphide.—When benzenyldiphenylamidine is heated with carbon disulphide at 130°–140°, there is formed thiobenzanilide and phenyl mustard oil.



The double bond is the point of attack with consequent loss of the imido group. Will and Beilschauski[2] have investigated the action of carbon disulphide upon the thiourea ethers.[3] They have shown, for instance, that methylthio-*p*-tolyl urea, heated with carbon disulphide at 180°, yields *p*-tolyl mustard oil and *p*-tolyldithiourethane,



a result analogous, in all respects, to that with a true amidine. Other thio-ethers behave in a similar manner.

Ethylisodiphenyl urea was heated with carbon disulphide at 170° for six hours. The tube opened with pressure due to combustible gases. These slowly precipitated silver sulphide from a silver nitrate solution due to the presence of carbonyl sulphide (COS). The contents of the tube, which consisted of a solid mixed with an oil, were washed out with ligroin. The solid, after crystallization from alcohol, proved to be thiocarbanilide. The ligroin, after evaporation, left an oil with the odor of phenyl mustard oil. That it was the mustard oil was proved by the fact that it reacted directly with alcoholic ammonia, giving

[1] Weith has shown that thiocarbanilide and hydrogen sulphide at 170° give a quantitative yield of aniline and carbon disulphide. *Ber. d. chem. Ges.*, 7, 1304.

[2] Bernthsen: *Ann. Chem.* (Liebig), 192, 32.

[3] *Ber. d. chem. Ges.*, 15, 1317.

monophenylthiourea, and with aniline to form thiocarbanilide.

Methyliso-*o*-tolyl urea was heated under like conditions with carbon disulphide. The tube opened with pressure due to inflammable gases that slowly precipitated silver sulphide. The contents of the tube consisted of *o*-tolyl mustard oil and *o*-thiocarbtoluide, which were separated and identified as in the previous experiment. If the reaction proceeded as with other amidines, it would be formulated as follows :

$$\text{I.} \quad \begin{matrix} \text{RNH} \\ \diagdown \\ \text{RN} \end{matrix} \!\!>\!\!\text{C}\!-\!\text{OC}_2\text{H}_5 + \text{CS}_2 \rightarrow \text{RNHCSOC}_2\text{H}_5 + \text{RNCS},$$

giving phenyl mustard oil ; and the β-thiourethane which was not isolated would have to break down according to

$$\text{II.} \quad 2.\text{RNHCSOC}_2\text{H}_5 \rightarrow (\text{RNH})_2\text{CS} + \text{COS} + (\text{C}_2\text{H}_5)_2\text{O}$$

into thiocarbanilide, carbon oxysulphide, and ether.[1]

The action on silver nitrate indicated carbon oxysulphide, and the correctness of this equation, and thereby of the whole interpretation, was proved as follows :

Pure β-thiophenylurethane[2] was heated in a sealed tube at 170°–180° for six hours. The tube opened with pressure due to inflammable gases that slowly precipitated silver sulphide from a silver nitrate solution. The contents consisted of a little phenyl mustard oil formed by simple dissociation of the urethane,

$$\text{C}_6\text{H}_5\text{NHCSOC}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{NCS} + \text{C}_2\text{H}_5\text{OH},$$

and of thiocarbanilide. The decomposition occurs as already pointed out in equation II.

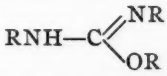
The same products were obtained when β-thiophenylurethane was heated in carbon disulphide solution. The experiments indicate that with a neutral reagent like carbon disulphide, the oxygen-urea ethers lose an imide group behaving, in all respects, like a true amidine.

The thiourea ethers react in this same way, the only difference being in the stability of the dithiourethane formed.

[1] Dithiophenylurethane, $\text{C}_6\text{H}_5\text{NHCSSC}_2\text{H}_5$, formed by the action of carbon disulphide on the thio-ethers, is stable at this temperature.—*Ber. d. chem. Ges.*, 15, 1317.

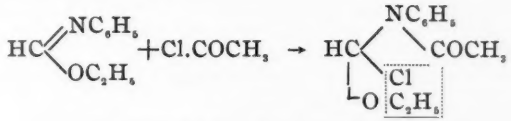
[2] The decomposition of the thiourethane will be further investigated and the results published in a later paper.

The Action of Acyl Chlorides upon the Urea Ethers.—Bodies of the type



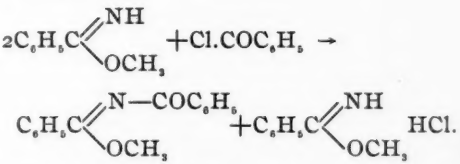
present toward acyl chlorides, two points of attack, the double bond and the hydrogen attached to the anilido group, which ought to be easily replaced by an acyl group, since the body is a strong base ; *i. e.*, anilidophenylimidoformic ether.

Wheeler and Walden[1] have made a most interesting discovery that the acyl chlorides act on phenylimido esters easily and smoothly, acetyl chloride giving with phenylimidoformic ester, acetylformanilide and ethyl chloride. They have formulated the reaction as follows :



$$\rightarrow (HCO)N(C_6H_5)(COCH_3)+ClC_2H_5.$$

On the other hand, they found that benzimidomethyl ester containing an imide group, NH, with a replaceable hydrogen atom reacts according to



The intermediate addition-product loses hydrogen chloride, which immediately unites with a second molecule of the more basic free imido ether to form a salt. The product then contains equal molecules of benzimidomethyl ester hydrochloride and benzoylbenzimidomethyl ester.[2]

If freshly distilled acetyl chloride (a slight excess over one molecule) is added to a benzene solution of ethyl isocarbanilide (one molecule), reaction soon begins. The use of a neutral sol-

[1] *Am. Chem. J.*, 19, 130.

[2] Wheeler and Walden : *Ibid.*, 19, 136.

vent is necessary in order to control the action. After standing for thirty-six hours, the benzene was filtered from a white solid that had crystallized out. This, on examination, proved to be pure carbanilide; there was no trace of any hydrochloride or salt of any base. The solution when evaporated directly yielded acetyldiphenylurea, a body previously described by McCreath.[1]

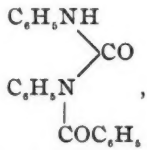
When ethylisodiphenylurea and benzoyl chloride are mixed, there is no reaction at first, but on standing for a short time, the mixture warms up and becomes semisolid. It is better, however, to dissolve the urea ether in benzene, add the benzoyl chloride, and allow the solution to stand two or three days. A white solid is slowly deposited; this, as in the previous case, was found to be pure carbanilide, with no admixture of any other body. The solution, on evaporation, gave a new compound, benzoyldiphenylurea, which was purified by recrystallization from ligroin (40°–60°) and alcohol.

Analysis:[2]

0.1027 gram substance gave 8.4 cc. moist nitrogen at 21.5° and 748.3 mm.

	Calculated for $C_{20}H_{16}N_2O_2$.	Found.
Nitrogen	8.86	9.18

Benzoyldiphenylurea,



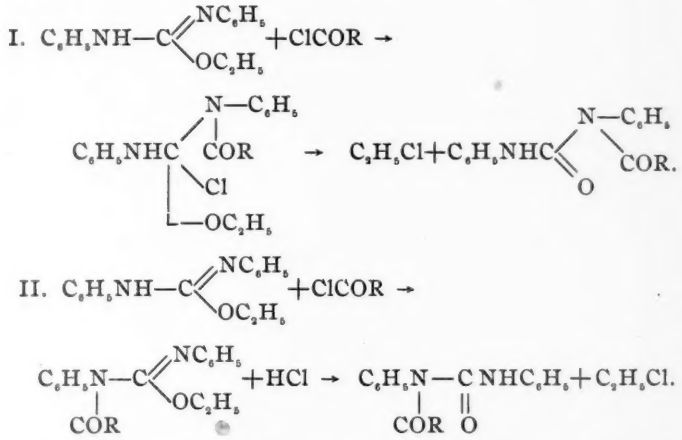
is insoluble in water, and easily soluble in ordinary organic solvents. It crystallizes in fine white needles, which melt at 131°. When heated a little above its melting-point, it dissociates, giving benzanilide and phenyl isocyanate, a reaction which also characterizes monacetylcarbanilide. These bodies, which can be prepared by the action of phenyl isocyanate upon the anilides,[3] are relatively unstable, and dissociate easily into their components.

[1] *Ber. d. chem. Ges.*, 8, 1181; Kuhn: *Ibid.*, 17, 2282.

[2] This analysis was kindly made for me by Mr. M. D. Slimmer, of this laboratory.

[3] McCreath: *Ber. d. chem. Ges.*, 8, 1181.

Since the isourea ethers possess two points of attack, the formation of these acyldiphenylureas can be explained in two ways:



In one the acyl chloride adds to the double bond, the usual point of attack in imido ethers, but the very unstable addition-product loses ethyl chloride, giving the monacyldiphenylurea. The formation of carbanilide is doubtless due to traces of free acid in the acyl chloride.[1] These results correspond in every way to the action of acid chlorides on the phenylimido ethers.[2]

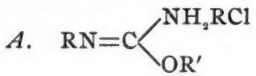
While the reaction most probably proceeded according to I, the second possibility had to be considered. Here the anilido hydrogen is replaced by the acyl group, while the free hydrochloric acid reacts with an acylurea ether, splitting off ethyl chloride and so giving the same end-products. The ease with which the urea ethers unite with dry hydrogen chloride has been set forth before. These hydochlorides are stable at ordinary temperatures in the absence of moisture.[3] For this reason, if any hydrochloric acid was set free, it would immediately unite with another molecule of urea ether to form the urea ether hydrochloride insoluble in the solvent used. This is shown also

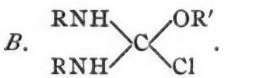
[1] Page 182.
[2] *Am. Chem. J.*, **29**, 130.
[3] Page 141.

by the behavior already referred to, of benzimidomethyl ester and benzoyl chloride.[1]

The absence of any hydrochloride of the urea ether or of any acyl urea ether leaves the second (II) interpretation of the action of acyl chlorides without a single experimental piece of evidence in its favor, and makes the first (I) the more probably correct one. The reaction is of some importance, since it must be considered as throwing some light on the constitution of the salts—such as the hydrochlorides— of the urea ethers.[2]

For these compounds two constitutions are possible:

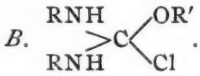




One would certainly think that if the basicity of the urea ethers was due to the aniline groups forming ammonium salts (A), that the basic anilido group, C_6H_5NH, would also show the other characteristic reaction of such a group in a basic molecule; *viz.*, the ready formation of an acyl derivative,

$$C_6H_5N(COC_6H_5)C(:NC_6H_5)OC_2H_5,$$

but no such compound could be obtained, although it was with the intention of preparing it, that this reaction was first undertaken and then studied. On the other hand, the formation of the compounds actually obtained,—acyl carbanilide and ethyl chloride—is according to I clearly in close agreement with the conception of the urea ether salts as having the constitution



Indeed where the imido ether grouping, —C(:NR)OR, is missing, acyl chlorides have hardly any effect. Thus, when carbanilide and benzoyl chloride are heated to 130°–140° in an oil-bath,

[1] Page 181.

[2] See also Stieglitz: *Am. Chem. J.*, 21, 101.

the diphenyl urea goes into solution, but on cooling it crystallizes out unchanged.[1]

V. CARBONYLDIURETHANE.

The urea ethers thus far investigated have a phenyl or tolyl group and are basic enough to form definite salts with, and neutralize, acids. It seemed now of interest to ascertain in what way the ethers of ureas would behave were the phenyl group replaced by one still more strongly negative, such as carbethoxy or acyl. Such a urea would possess the grouping,

$$RCONHCONHCOR,$$

analogous to that in the uric acids, and, in consequence, its reactions should throw some light upon those of the latter series.

A starting-point for the preparation of ethers of such a urea presents itself in carbonyldiurethane,

$$CO(NHCOOC_2H_5)_2$$

(dicarbethoxyurea), a compound whose constitution has been definitely determined, so that no question need arise on that score. This body, together with its silver salt, was prepared in this laboratory,[2] by Folin, who worked under the direction of Dr. Stieglitz. He found that carbonyldiurethane gave a monosilver salt, probably

$$(AgO)C(:NCOOR)(NHCOOR).$$

Such a body would present an excellent opportunity for preparing such isourea ethers by means of alkyl iodide, and on the other hand, the formation of such ethers with the constitution

$$(RO)C(:NCOOR)(NHCOOR),$$

would be a complete confirmation of the constitution of the silver salt. With this twofold object, the action of alkyl iodide was investigated by me.

An isourea ether with the above composition was obtained without difficulty, its constitution determined beyond a doubt, and important changes in the chemical behavior of isourea

[1] At higher temperatures (160°-170°) there is a reaction, the results of which will be described in a later paper. The study of the action of acyl chlorides and anhydrides on the dialphylureas and thioureas, is being continued by me (Dains).

[2] *Am. Chem. J.*, 19, 348.

ethers, with the more negative carbethoxy groups, COOR, attached to the nitrogen observed.

Preparation of Carbonyldiurethane.—Folin ascertained that carbonyldiurethane was the main product when a mixture of one molecule of phosgene, two molecules of urethane, and two molecules of pyridine were heated in a sealed tube at 85° for thirty minutes. A more simple method of preparation, and one that does not involve the use of a sealed tube, is as follows: A mixture is made of two molecules each of urethane and pyridine; a little benzene is used, if necessary, to complete the solution. A flask containing a ten per cent. solution of phosgene (one molecule), in benzene and connected with an ice-cooled condenser, is surrounded with a freezing-mixture. On adding the urethane solution slowly to the phosgene, immediate reaction occurs, and a reddish solid separates out on the sides of the flask. After standing an hour the freezing-mixture is replaced by water, which is slowly warmed to the boiling-point of benzene. This latter temperature is maintained for an hour. When cold, the liquid in the flask separates into two layers, the upper of benzene, the lower a dark red oil which slowly becomes semisolid, owing to the crystallization of the carbonyldiurethane. On examination, the upper layer was found to contain very little carbonyldiurethane, the most of it being in the red oil at the bottom. This latter, after treatment with water, was warmed to drive off traces of benzene, and cooled in a freezing-mixture, the carbonyldiurethane readily crystallizing out. On concentrating the filtrate and again cooling, a second crop of crystals can be obtained while extraction with ether removes the remainder. The product is best purified by crystallization from water. The yield is about seventy per cent. of the theory. With a sealed tube Folin had obtained a forty per cent. yield. The presence of the pyridine, which absorbs the hydrochloric acid set free, greatly facilitates the reaction. A benzene solution of phosgene and urethane alone does not react at the boiling-point of the benzene.

Carbonyldiurethane is very stable toward acids.[1] Fixed caustic alkalies dissolve it with the formation of soluble salts. For synthetic use the silver and sodium salts of carbonyldiureth-

[1] Folin: *Am. Chem. J.*, 19, 348.

ane were prepared, the first by Folin's method,[1] the latter as follows:

A concentrated solution of sodium ethylate—one molecule—was added to a solution of carbonyldiurethane, dissolved in as little absolute alcohol as possible. A gelatinous precipitate formed, which soon changed to a fine white crystalline powder. From more dilute solutions ether throws down the sodium salt. This was washed with absolute alcohol and ether, dried in a vacuum, and analyzed.

0.5800 gram substance gave 0.1790 gram sodium sulphate.

	Calculated for $C_7H_{11}N_2O_5Na$.	Found.
Sodium	10.18	10.00

No Disodium Salt Could be Obtained.—The monosodium salt, is formed only with a considerable excess of sodium ethylate. It is readily soluble in water and dilute alcohol. From a concentrated water solution of the sodium salt, lead nitrate precipitated the lead salt, but as this was found to be very unreactive with alkyl iodide, it was not further investigated.

With copper sulphate it gave not copper carbonyldiurethane, but a hydrated copper hydroxide, showing that the sodium salt is hydrolyzed in solution. The constitution of these salts will be discussed later.

The Action of Alkyl Iodide upon the Silver Salt.—The silver salt was suspended in dry ether and a slight excess over one molecule of ethyl iodide added. After standing for several days the ether was filtered from the silver iodide. On evaporation there is obtained an oil mixed with a little carbonyldiurethane. The oil was purified by washing with dilute alkali, and by solution in ligroin (b. p. 40°–60°), which dissolves only the oil. The excess of solvent was allowed to evaporate in a vacuum desiccator over vaseline and sulphuric acid. The resulting product is the ethoxy ether of carbonyldiurethane,

$$(C_2H_5O)C(:NCOOC_2H_5)NHCOOC_2H$$

(ethylisodicarbethoxyurea). It is a colorless mobile oil with a pleasant odor, easily soluble in ordinary neutral organic solvents, insoluble in water and insoluble in dilute alkalies. At ordinary

[1] Folin: *Am. chem. J.*, 19, 350.

pressures it cannot be distilled without complete decomposition.

Analysis:

0.2444 gram substance gave 26.8 cc. moist nitrogen at 24° and 755 mm.

	Calculated for $C_9O_5H_{16}N_2$.	Found.
Nitrogen.....	12.07	12.30

Traces of the isomeric nitrogen ether are often found, showing that the reaction is not wholly one of direct replacement of the silver atom. If any nitrogen ether is present a carbylamine odor is obtained when the ether is decomposed with strong sulphuric acid and then warmed with alcoholic potash and chloroform. That the composition of the oil is

$$\begin{array}{l} HN—COOC_2H_5 \\ \quad | \\ \quad C—OC_2H_5 \\ \quad \| \\ \quad N—COOC_2H_5 \end{array}$$

(ethylisodicarbethoxyurea) is shown by its reactions with hydrochloric acid and alcoholic ammonia.

Action of Hydrochloric Acid on Ethylisodicarbethoxyurea.—When dry hydrogen chloride is passed over the ethoxy ether in a test-tube connected with an azotometer, ethyl chloride is split off quantitatively and is collected in the azotometer over caustic potash. It was identified by its burning with a green flame.

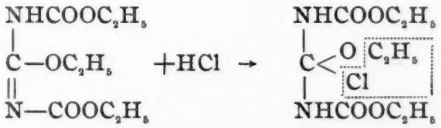
The reaction begins in the cold and is accompanied with heat. Cooling the ether in a freezing-mixture does not prevent it. The residual solid was found to be carbonyldiurethane. This renders certain the presence of a third ethoxy group bound to carbon, C—OR, other than the two ethoxy groups in carbonyldiurethane itself, since hydrogen chloride at ordinary temperatures cannot split off alkyl chloride from a nitrogen alkyl derivative,

$$>N—C_2H_5,$$

and since carbonyldiurethane is recovered undecomposed. The same decomposition takes place with dilute aqueous hydrochloric acid, slowly in the cold, rapidly on heating. Carbonyldiurethane seems to be the only solid product of the reaction.

Efforts were made to isolate the hydrochloric acid addition

product by passing the dry gas into a well-cooled benzene solution of the ether, but with no success. Carbonyldiurethane was alone obtained.



It will be noticed that the stability of the hydrochloric acid addition products decreases with the acidity of the ethers. Thus, while ethyliso-*o*-carbtoluide hydrochloride in a stream of dry hydrogen chloride loses ethyl chloride only at 90°, the more negative ethoxycarbethoxyurea reacts with hydrogen chloride even at 0°.

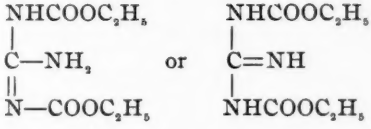
Action of Alcoholic Ammonia.—The ethoxy ether was dissolved in strong alcoholic ammonia. After a few moments' standing a fine, white precipitate formed. This melted at 163° and proved to be identical with guanidinedicarboxylate obtained by Nenki[1] from guanidine and chlorcarbonic ether. The compound obtained from ethylisodicarbethoxyurea dissolved readily in dilute hydrochloric acid, and with chlorplatinic acid gave a salt which afforded still further proof of its identity.

I. 0.1324 gram substance gave 0.0316 gram platinum.

II. 0.1562 gram substance gave 0.0374 gram platinum.

	Calculated for $C_{14}H_{28}O_8N_6PtCl_6$.	Found. I.	II.
Platinum.....	23.91	23.87	23.94

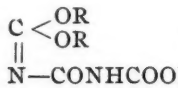
Guanidinedicarboxylatechlorplatinate forms hard, red crystals, readily soluble in water. It does not melt at 250°. The formation of this dicarbethoxyguanidine,



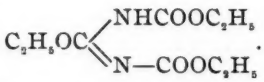
is of great importance, since it proves definitely that the third

[1] *J. prakt. Chem.* (2), 17, 237.

ethoxy group in ethyl isodicarbethoxyurea is bound to the central carbon atom; that is, the constitution cannot be



These two reactions, with hydrogen chloride and with ammonia, have shown the presence of an ethoxy group and also its position; in other words, have definitely proved the constitution of the molecules to be



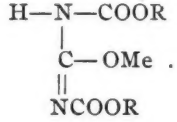
Ethoxycarbonyldiurethane is insoluble in water and in the dilute fixed alkalies, and is not readily decomposed by them. In this respect it bears a close resemblance to the dialphylurea ethers. At the same time, the replacement of an alphyl group by the more negative carbethoxy has increased greatly its reactivity.

The exceeding ease with which ethoxycarbonyldiurethane splits off ethyl chloride with hydrogen chloride, and forms a guanidine derivative with alcoholic ammonia, is in strong contrast to the alphylurea ethers, whose chlorides are relatively stable, and which do not react with alcoholic ammonia below 180°.

As has been pointed out above, this work has a very interesting bearing upon the constitution of the metallic salts of carbonyldiurethane. Since the ethoxydicarbethoxyurea has been shown to have the structure

$$C_2H_5OC(:NCOOR)(NHCOOR),$$

it follows that the silver salt, and hence the other metallic derivatives, must have an analogous constitution, and be represented as follows:



This structure shows, too, why the ether, though it contains an NH group, is insoluble in alkalies, and why only a monosilver or sodium salt of carbonyldiurethane can be formed.

The investigation of the action of ethyl iodide upon the sodium salt is now being carried on by me. Results already obtained show that when the sodium salt suspended in dry ether is heated with ethyl iodide at 160°, nitrogen, and not oxygen, ethers are formed. Two products were isolated—one an oil which gave a carbylamine reaction and resembles in its properties diethylurethane,

$$C_2H_5NHCOOC_2H_5;$$

the other, a solid melting at 91°–92°, insoluble in alkalies, but readily soluble in organic solvents, which also responds to the carbylamine test.

In studying the properties of carbonyldiurethane, the action of ammonia was tried with some interesting results. Carbonyldiurethane was heated with alcoholic ammonia in a sealed tube at 100°, for several hours. The product, on examination, proved to be allophanic ether, showing that saponification had occurred, instead of the normal amide reaction,

$$CO(NHCOOC_2H_5)_2+H_2O \rightarrow NH_2CONHCOOC_2H_5+CO_2+C_2H_5OH.$$

Sodium ethylate, in one case, had the same action.

Different results were obtained when the carbonyldiurethane was heated at 100° with twenty-eight per cent. ammonia. The clear solution, after evaporating off the excess of ammonia, deposited crystals. These heated to 180°–190° partially decomposed with the evolution of a gas, and the formation of a white solid which did not melt on further heating. This same body is obtained by the action of concentrated ammonia in the cold. While the compound was not analyzed, its reactions indicate that it is the ammonium salt of carbonyldiurea,

$$CO(NHCONH_2)_2,$$

which acts like a dibasic acid.

This conclusion is based on the following facts:

a. Its partial decomposition at 190° into a gas and a residual solid.

b. Warming gently with dilute caustic soda gives free ammonia. Carbonyldiurea or biuret is decomposed only with difficulty by caustic alkalies.

c. Dilute acids throw down a precipitate which corresponds in its properties to the carbonyldiurea prepared by Schmidt.[1]

That carbonyldiurea acts as a dibasic acid was shown by the preparation of its silver salt. A solution of the ammonia salt of carbonyldiurea was added to two molecules of silver nitrate. This formed immediately a fine, heavy, white precipitate, which was filtered, washed with dilute ammonia and hot water, and analyzed.

I. 0.2686 gram substance gave 0.1620 gram silver.

II. 0.1958 gram substance gave 0.1182 gram silver.

	Calculated for $C_2O_2H_4N_4Ag_2$.	Found. I.	II.
Silver.....	60.00	60.31	60.36

The disilver salt is very stable and is discolored only slowly on exposure to the light.

When equal molecules of silver nitrate and carbonyldiurea were mixed no monosilver salt was obtained, but only the disilver compound.

I wish to take this opportunity to thank Prof. Stieglitz for his valuable direction and kindness in the prosecution of this work.

KENT CHEMICAL LABORATORY,
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THE NATURE OF VALENCE.

BY F. P. VENABLE.[2]

Received December 31, 1898.

THE term "valence" is variously defined as the "combining capacity", "capacity of saturation", "quantitative combining power", or "chemical value of the atom." It is well known that the introduction of this idea into chemistry was due to the development of the type theory, a system which had at first a purely empirical basis. Sixty years ago there was still some hesitation as to the acceptance of the atomic theory or the need for such a theory. Much use was made of the term equivalent, which had been Wollaston's expedient for avoiding

[1] *J. prakt. Chem.* [2], 5, 39.

[2] Address, as chairman, delivered before the North Carolina Section.

the difficulties arising from the full adoption of the theory of atoms.

Wollaston had been himself very far from consistent in the use of the term. The numbers called by him 'equivalent weights' were not infrequently atomic and molecular weights and fully as hypothetical as the so-called atomic weights of Dalton. In the later use of the term it signified solely the numbers obtained by analysis without the introduction of any theoretical considerations. Thus, on analyzing ammonia, the ratio

$$N : H :: 4.6 : 1,$$

is gotten, and therefore the equivalent of nitrogen is 4.6. Strange to say the equivalent given by Wollaston corresponds with the present atomic weight, whereas the atomic weight given by Dalton corresponds with what would be the equivalent.

It is manifest that the idea of equivalents needed something more than the simple theory of atoms to make it clear and tenable. It embodied two distinct conceptions and if we hold to an atomic theory we must introduce a further explanatory theory of the saturation capacity of these atoms. This is the theory of valence or quantivalence or atomicity, and without it the equivalents are purely empirical, and it is most difficult if not impossible to clear up the confusion connected with their use.

Returning now to the derivation of this idea of valence from the type theory, according to Wurtz[1] the conception of valence was introduced into the science in three steps. First there was the discovery of polyatomic compounds. This term was first used by Berzelius in 1827[2], he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. The term was later applied by Graham, Williamson, and others to compounds.

The second step was the reference of this polyatomicity to what was called the state of saturation of the radicals contained in these compounds. This was largely through the work of Williamson and Gerhardt.

Thirdly this conception of saturation was extended to the elements themselves. This was chiefly due to the work of Frank-

[1] Histoire des doctrines chimiques, p. 69.
[2] *Jsb. d. Chem.*, 7, 89.

land upon the organo-metallic compounds. And so valence has come to refer to the number of atoms with which a single atom of any element will combine.

This conception has then been one of slow growth, gradually incorporating itself into the science as the necessity arose of devising a suitable explanation for accumulated observations. It was a logical outcome of and was evolved from knowledge acquired step by step. It was no mere speculation or hypothesis, such as that of Prout, evolved by the brilliant fancy or imagination of one man and suddenly appearing with scarcely a claim to foundation upon observed fact.

This conception enters into the chemical theory of to-day almost as fundamentally as the atomic theory itself. Its application is of every-day occurrence and of the most varied character, and yet chemists admit that the nature of valence is one of their chief puzzles and they have advanced but little towards its solution during the past half century. It is quite possible that the ideas to be advanced in the further discussion of this subject in this paper will meet with antagonism. Certainly they should be fully and freely discussed if they are worthy of it. I believe that they form a step toward the clearing up of the mystery of valence.

It is necessary, however, first to trace somewhat further the development of the original conception. One of its earliest and most important applications was to the study of the constitution of the compounds of carbon. Here Kekulé assumed for carbon a constant valence of four, and this idea is still dominant in theories relating to the constitution of these bodies. It was quite natural then that the first belief should have been in a constant valence. It was speedily found, however, that in certain cases, as in the compounds of nitrogen and phosphorus, this belief was scarcely tenable. There were efforts at making it hold good, as, for instance, a distinction was drawn between atomic and molecular compounds, but all of these suggestions have been proved unsatisfactory.

We unquestionably have to account for the existence of a compound with three atoms and another with five atoms in the cases of nitrogen and phosphorus and there are many similar anomalies. Here the valence seems to vary toward one and the same

element. Cases might be multiplied to show also that it varies often towards different elements. Thus it frequently happens that the valence of an element towards hydrogen seems to be quite different from that exhibited toward oxygen. For a long time there was much straining to consider the valence of an element always the same but this effort is, in large measure, abandoned now as unavailing and chemists admit that valence is not constant but variable and may even vary towards one and the same element.

The doctrine of valence has had much added to it about bonds, affinities, and linkage, the necessity for which one may well question. Certainly the misuse of the word affinity here, seeing its other and greater use, should be earnestly discountenanced. I am inclined to think that the other terms bring in false and misleading ideas which should be carefully guarded against. At any rate all hypothetical talk about strong bonds, and weak bonds, double bonds and triple is to be avoided.

If then valence varies, can it be an inherent property of the unchanging atoms? Experiments have shown that it varies with the nature of the combining element, that it varies with the temperature and with other conditions. It is not dependent upon the atomic weight in the same sense as other properties are dependent upon it. Thus in the same group the valence remains the same whether the atoms weigh nine times as much as hydrogen or two hundred times as much.

We seem shut up to the conclusion that valence is not one of the primitive inherent properties of the atom but is relative. It is rather to be regarded as the resultant of the mutual influence of the atoms of the combining elements. The clear grasping of this idea is an important step forward. Unfortunately the distinction is not always made nor consistently adhered to.

It may not be amiss to cite here the utterances of Lothar Meyer in regard to the question of a constant or variable valence.[1]

"Since the aim of all scientific investigation is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors, then it is clear that

[1] Modern Theories of Chemistry, Eng. Trans , p. 303.

chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable leads to no advancement.

"The first step towards progress in this matter would be made if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realized. While some chemists, accepting the the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked, that an arbitrary interpretation carried out by means of chosen hypotheses, cannot be regarded as an attempt at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element in different compounds, should be traced to a distinct cause. If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter, for such a statement is merely a paraphrase which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the past few years that similar paraphrases have not only been proposed but also accepted as real explanations of such phenomena. Just as it was formerly supposed that the assumption of a vital force dis-

pensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency', a means of explaining the varying stoichiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom and like it invariable; or whether this ability is variable and with it the nature of the atom itself."

It is not strange that this line of reasoning should lead Lothar Meyer to doubt the unvarying nature of the atom itself, and thus losing his grasp upon one invariable to make sure of another. He says: "It is by no means impossible that the magnitudes which we now style atoms, may be variable in their nature."

It will be an unfortunate day for chemists when the belief in the unchanging atom is given up. Chaos will indeed enter into all of our theories when this, the foundation rock, is left at the mercy of every shifting tide of opinion and can be shaken by all manner of unfounded hypotheses.

The case cannot be so hopeless as to necessitate calling to our aid so dangerous a doctrine. Before turning to such an expedient let us first make all possible use of our atomic theory as it stands. The extension of this theory teaches that the atoms are endowed with motion and this motion probably varies in velocity and phases with the different elements. So too when the atoms unite the resulting molecule has a certain motion peculiar to it while the atoms composing it have an intra-molecular motion in which their original motions are probably modified by their influence upon one another. It is quite manifest then that a molecule, in order to exist, must maintain a certain equilibrium and harmony between these various motions, and that there can be all degrees of equilibrium from the very stable to that which may be upset by the least disturbing influence from without.

It seems to me that herein we have a full and satisfactory means of explaining the various problems connected with the conception of valence. The question as to whether the atoms of two elements will unite is decided by affinity, which is in some

way connected with the electrical condition of those atoms. There is no apparent connection between this and valence. The number of atoms which enter into combination forming one molecule is purely a matter of equilibrium and is dependent upon the motion of those atoms. Thus a phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of harmonizing the respective motions. As the temperature may affect these motions and also impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend upon the temperature and that a temperature may be reached at which no harmony is possible and hence no compound can be formed. The phosphorus atom mentioned can, as we know, form a stable molecule with five atoms of chlorine. On increasing the temperature this becomes unstable and only three atoms can be retained. Neither with four atoms nor with two is there harmony of motion. A sufficiently high temperature may prevent any harmony of motion whatever being attained and hence union may become impossible.

As to other influences than those of temperature, we can see that the equilibrium between the atom of phosphorus and the five atoms of chlorine may be upset by such a molecule coming within the influence, electrical or vibratory, of a molecule of water. The atoms must rearrange themselves for a new state of equilibrium and so an atom of oxygen takes the place of two atoms of chlorine, giving again a condition of harmony. In other cases the motion of the molecule of water may be of such a character as to directly harmonize with that of the original molecule and so to enter into equilibrium with it, a definite number of such molecules of water affording a condition of maximum stability. This we call water of crystallization. Such molecules would be more or less easily separated by an increase of temperature and where several molecules of water were attached the highest temperature would be necessary for freeing the original molecule from the last water molecule.

A carbon atom finds its most perfect state of equilibrium where four atoms of hydrogen or their equivalents move in harmony with it. But there is a second state of equilibrium where only

half that number of atoms are moving with it. This state does not seem to be a possibility where these are hydrogen atoms but is readily possible where the equivalent number of oxygen atoms is concerned. Such a molecule, however, is always in a condition to take up additional atoms until its highest equilibrium is reached and in doing this it proceeds by the regular steps needed for bringing about a harmony of motion. A molecule in a lower state of equilibrium we have become accustomed to call unsaturated, calling that one saturated which is in its highest state of equilibrium. The further application of this hypothesis is easily made and need not be dwelt upon here. It will be helpful in many ways.

This theory of valence makes it clear why it should vary toward the same element under different conditions. It is also clear that it might vary towards different elements as these are very possibly possessed of different motions. It is further evident that it is in accord with the conclusion that valence is not an inherent property of the individual atom but is the resultant of the influence upon each other of the combining atoms.

Only one point remains to be considered: Why do the elements of the same group have practically the same valence? The nearest answer to this, and it seems satisfactory, is that they are all possessed of the same phase or kind of motion. In other words the natural division into periods gives us seven or eight more or less different phases. These are, in large measure, independent of the atomic weight. And so the elements in any given group have the same tendency towards similar states of equilibrium in forming compounds with any other element, as hydrogen or oxygen. Some elements, as copper, mercury, tin, etc., are peculiar in that they may change their phase of motion under certain influences, acting then as if they belonged to different groups and entering into totally different states of equilibrium in forming their compounds.

Lastly it is possible for a combination of atoms of different elements, as NH_4 or CN, to have such molecular and intra-molecular motion that, although not in a state of equilibrium themselves, they are capable of entering into such states just as the single atoms of elements do, having apparently similar valence.

I might develop this theory much further but it is unnecessary

now. Enough has been said to show that such an application of the atomic theory is legitimate and is most highly important as a step towards the clearing up of the problems springing from the conception of valence and from the periodic system.

Note.—Since certain points in this paper require treatment at greater length than was practicable in an address, it will be followed by a second paper elaborating such portions.

UNIVERSITY OF NORTH CAROLINA, December 29, 1898.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1898.

BY F. W. CLARKE.

Received January 10, 1898.

DURING the year 1898, there has been an increased activity in the determination of atomic weights, and a considerable number of investigations have been published. The importance of the subject is also indicated by the fact that the German Chemical Society has appointed a strong committee to report annually upon atomic weights; and its action for the current year is stated farther on. The new data are as follows:

OXYGEN.

Keiser[1] has effected the complete synthesis of water, by a new method, in which the hydrogen held by palladium, the oxygen, and the water produced are all determined by successive weighings in one and the same apparatus. For details of construction, etc., the original memoir must be consulted. The data for four experiments are as follows:

Weight H.	Weight O.	Sum H + O.	Weight H_2O.
0.27549	2.18249	2.45798	2.45975
0.27936	2.21896	2.49832	2.49923
0.27091	2.15077	2.42168	2.42355
0.26845	2.13270	2.40115	2.40269

From columns first and second, the ratio H : O can be computed, while the first and fourth give the ratio H : H_2O.

Ratio H : O.	Ratio H : H_2O.
7.922	8.929
7.943	8.946
7.939	8.946
7.944	8.950
Mean, 7.937	Mean, 8.943

From ratio H : O, O = 15.874
" " H : H_2O, O = 15.886

Mean, 15.880

[1] *Am. Chem. J.*, 20, 733, November, *1898*.

This value is very near that obtained by Morley, 15.879; and has corroborative value. Its great merit is in the directness of the determination, and in the avoidance of complicated or troublesome corrections.

NITROGEN.

The equivalent of cyanogen has been determined by Dean;[1] but as yet only an abstract of his work has appeared. Silver cyanide was dissolved in nitric acid, and titrated by Stas' method with potassium bromide. The data give CN = 26.065; whence, if C = 12.01, N = 14.055.

BORON.

Armitage[2] has redetermined the atomic weight of boron by two methods. First, by determination of the percentage of water in borax, which had been washed with alcohol and ether successively, and then dried for six hours in a vacuum. The mean of six experiments gave

$$B = 10.959.$$

Secondly, by the method of Rimbach. Fused borax was dissolved in water and titrated with dilute sulphuric acid. The mean of two experiments gave

$$B = 10.928.$$

The abstract published gives no details of individual determinations, and neglects to state what values were assigned to the other atomic weights involved in the calculations, except that O = 16. The communication was discussed, in the main unfavorably, by Veley, Groves, Scott, and Dewar.

Armitage's paper called forth also a brief note from Leonard,[3] who refers to experiments of his own upon the dehydration of borax. He states that soda and boric acid are both volatilized when borax is intensely ignited, and that the composition of the residue is not constant. From this he concludes that the use of borax for determinations of atomic weight is liable to be attended by serious errors.

[1] *Chem. News*, 78, 261, November 25, *1898*.
[2] *Ibid.*, 77, 78. A paper read before the Chemical Society. Not yet printed in full.
[3] *Ibid.*, 77, 104.

ZINC.

In the atomic weight determinations made some years ago by Morse and Burton, metallic zinc was converted into oxide, and in that way the ratio between metal and oxygen was measured. Later, Richards and Rogers showed that zinc oxide, prepared as Morse and Burton had prepared it, namely, by conversion of the metal into nitrate and subsequent ignition, always retained occluded gases, and in distinctly weighable quantities.

The research is now completed by the labors of Morse and Arbuckle,[1] who have repeated the determinations made by Morse and Burton, with measurements of the occluded gases, and correction for them. In each experiment the gas, which consisted of oxygen and nitrogen, was analyzed; and the corrections applied assume the liter weights to be, under standard conditions at latitude 45° and sea-level, 1.42923 grams for oxygen, and 1.25461 for nitrogen. The volumes are given in cubic centimeters.

Weight Zn.	Weight ZnO.	Volume gas.	Per cent. O.	Atomic weight Zn.
1.19573	1.48860	0.468	26.28	65.459
1.03381	1.28707	0.402	18.14	65.445
1.06519	1.32599	0.342	18.42	65.459
1.05802	1.31711	0.312	18.58	65.440
1.26618	1.57619	0.521	13.82	65.489
1.03783	1.29198	0.408	35.28	65.475
1.08655	1.35276	0.412	19.55	65.437
1.11364	1.38647	0.456	18.62	65.447
			Mean,	65.457

O = 16. Vacuum weights are given. Without correction for occluded gases, Zn = 65.328, as against the earlier determination of Zn = 65.27. The new determinations agree closely with those of Richards and Rogers, who found Zn = 65.459, and of Richards alone, who found Zn = 65.404. The value assigned to zinc in the table of your committee is 65.41, as published a year ago.

CADMIUM.

In the case of cadmium the same uncertainty existed as in the case of zinc. Morse and Jones had determined the atomic weight by conversion of the metal into the oxide, in that way

[1] *Am. Chem. J.*, **20**, 195, March, *1898*.

finding Cd = 112.06. Morse and Arbuckle[1] have repeated the investigation, this time with search for occluded gases in the oxide, and now give a new series of data, with corrections applied. In all essential features the research is parallel to that upon zinc, which had just been noted; and the results obtained are given in the subjoined table. The weights are reduced to a vacuum, and O = 16.

Weight Cd.	Weight CdO.	Volume of gas.	Per cent. O.	Atomic weight Cd.
1.93188	2.20764	0.574	21.25	112.392
1.67935	1.91910	0.480	25.16	112.365
1.48430	1.69620	0.441	19.95	112.376
1.36486	1.55972	0.402	18.33	112.368
1.50295	1.71744	0.419	21.95	112.394
1.43804	1.64330	0.431	18.56	112.395
1.44041	1.64604	0.406	20.93	112.365
1.45938	1.66771	0.421	21.85	112.375
1.40379	1.60420	0.390	19.50	112.359
			Mean,	112.377

The uncorrected weighings give Cd = 112.084. Bucher, working with cadmium chloride and cadmium bromide, found the mean values 112.39 and 112.38, and the analysis of cadmium sulphate gave 112.36. These results accord fairly well with the determinations made by Dumas and by Huntington, but not with those of Hardin. The weight of evidence, however, now seems to be with the higher value, which may, with much probability, be adopted.

COBALT AND NICKEL.

The paper by Winkler[2] upon these metals is merely a criticism of the determinations by Richards and Baxter, and Richards and Cushman, which were noticed in the committee report for 1897. No new determinations are offered. Winkler suggests that the bromides prepared by Richards and his associates, which were sublimed in porcelain tubes, might have acted upon the glaze of the latter, and so have acquired impurities. He also suggests that perhaps the bromide might have retained an excess of hydrobromic acid, and he points out possible danger in the use of the Gooch crucible, in which the silver bromide was collected.

[1] *Am. Chem. J.*, 20, 536, July, *1898*.
[2] *Ztschr. anorg. Chem.*, 17, 236, June 25, *1898*.

SELENIUM.

The atomic weight of selenium has been redetermined by Lenher,[1] in the laboratory of the University of Pennsylvania. First, silver selenite was heated in a stream of gaseous hydrochloric acid, giving silver chloride, the latter being quite free from selenium. Three experiments gave as follows:

Weight Ag_2SeO_3.	Weight AgCl.	Atomic weight Se.
0.98992	0.82715	79.326
1.59912	1.33600	79.373
2.70573	2.26087	79.320
	Mean,	79.339

In a second series of eight experiments the silver chloride, after weighing, was reduced to metal in a stream of hydrogen. Thus the ratio between silver selenite and silver was measured. The weighings were as follows:

Weight Ag_2SeO_3.	Weight AgCl.	Weight Ag.
0.26204	0.21897	0.16480
0.58078	0.48522	0.36534
0.70614	0.58999	0.44417
0.80811	0.67532	0.50821
0.98396	0.82232	0.61882
1.29685	1.08350	0.81562
1.63103	1.36288	1.02588
2.00162	1.67234	1.25884

Hence, for the atomic weight of selenium we have:

Ag_2SeO_3 : AgCl.	As_2SeO_3 : Ag.
79.299	79.356
79.371	79.280
79.350	79.301
79.282	79.369
79.263	79.358
79.361	79.277
79.316	79.320
79.358	79.357
Mean, 79.325	Mean, 79.329

Still another set of determinations was based upon analyses of ammonium bromoselenate, Am_2SeBr_6. This salt was reduced by hydroxylamine hydrochloride, and the precipitated selenium was weighed in a Gooch crucible. The results are subjoined:

[1] This Journal, **20**, 555, August, *1898*.

Weight Am_2SeBr_6.	Weight Se.	Atomic weight Se.
1.00059	0.13324	79.243
1.50153	0.20022	79.367
2.00059	0.26649	79.273
2.00126	0.26657	79.269
3.00125	0.39958	79.226
4.00216	0.53346	79.333
5.00218	0.66656	79.306
5.03001	0.66998	79.267
	Mean,	79.285

General mean of all twenty-seven determinations,

$$Se = 79.314.$$

The antecedent values are $O = 16$, $H = 1.008$, $N = 14.04$, $Ag = 107.92$, $Br = 79.95$, $Cl = 35.45$. All weights were reduced to a vacuum.

The result obtained is near that found by Dumas, but considerably higher than that given by Ekman and Pettersson. The reason for this disaccordance is yet to be found. In the table at the end of this paper the value assigned to selenium is the mean of Lenher's determination, and the value given in the report of last year ; namely, when $O = 16$,

$$Se = 79.17.$$

Neither the new nor the old determinations can be yet adopted to the exclusion of the other, and the mean value is the safest for present use.

TELLURIUM.

Metzner[1] has employed two methods for determining the atomic weight of this element. First, by synthesis of the sulphate, Te_2SO_7, which is perfectly stable at 440°. The tellurium which served as the starting-point was prepared by dissociation of hydrogen telluride, and was crystallized in beautiful needles. By solution in sulphuric acid, evaporation to dryness, and calcination at temperatures not over 440°, the sulphate was produced. The weights given are probably milligrams.

Weight Te.	Weight sulphate.	Atomic weight Te.
790.2	1235.0	127.9
414.3	647.5	128.0
1098.3	1717.0	127.8

[1] *Ann. chim. phys.* [7], 15, 272, October, *1898*.

Metzner's second method consisted in reducing tellurium dioxide by carbon monoxide, in presence of metallic silver. The latter prevents the volatilization of tellurium.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
743.2	118.8	127.8
1106.7	221.3	128.0
988.5	197.0	128.24
1312.5	263.0	127.75

Metzner adopts 127.9 as the final result of his investigation. Apparently his weights were not reduced to a vacuum, and he neglects to state what value he assumed for the atomic weight of sulphur. O = 16 was evidently the basis of his calculations.

The work of Metzner called forth two theoretical papers by Wilde,[1] who holds that the experiments show that the true value for tellurium is 128. In his second paper he discusses the positions of tellurium and iodine in the periodic system. As both communications are purely critical in character, and contain no new data, they need no further notice here.

Still another set of determinations relative to tellurium is due to Heberlein.[2] First, telluric acid was dissolved in hydrochloric acid, and the liberated chlorine was distilled off into a dilute solution of potassium iodide. In the latter, iodine was set free, and was titrated with a decinormal solution of sodium thiosulphate. The values found for Te, with O = 16 and H = 1.008 are

127.16
127.28
127.32
127.35
127.09

Mean, 127.24

Secondly, telluric acid was transformed into tellurium dioxide, by heating with proper precautions to avoid loss.

Weight $H_2TeO_4.2H_2O$.	Loss of weight.	Atomic weight Te.
1.35236	0.41431	126.60
1.76859	0.54122	126.84
		Mean, 126.72

[1] *Compt. rend.*, **127**, 613, 616.

[2] Beitrage zur Kenntnis des Tellur's.—Doctoral Dissertation: Strassburg, 1898.

Thirdly, tellurium dioxide was reduced to tellurium by means of hydrogen, in presence of metallic silver.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
1.35908	0.37353	126.99
1.94038	0.39050	127.00
		Mean, 126.995

The mean of all three series is Te = 126.985.

It will be seen that some of these values range below, and others above, the atomic weight of iodine. Heberlein regards the higher figures as too high, and the lower as probably too low, the mean of all being most nearly correct. The main question, the position of tellurium in the periodic system, he considers experimentally unsettled, but favors the opinion that more critical determinations will place it below iodine and in the sulphur-selenium group. The value which he has actually found is only a trifle higher than that of iodine, and better determinations may well reduce it to the necessary amount.

ZIRCONIUM.

Venable[1], in order to determine the atomic weight of this element, has availed himself of the oxychloride, $ZrOCl_2.3H_2O$. This compound can be crystallized from strong hydrochloric acid, and dried in a current of gaseous hydrochloric acid at 100°–125° without loss of its water. When dissolved in water in a platinum crucible, evaporated to dryness, and strongly ignited, pure zirconia, free from chlorine, remains. The ratio $ZrOCl_2.3H_2O : ZrO_2$ is thus determined, and from it the atomic weight of the metal is calculable. The results of ten experiments are given by Venable, as follows:

Weight $ZrOCl_2.3H_2O$.	Weight ZrO_2.	Ratio.
5.25762	2.78450	52.961
3.53994	1.87550	52.981
3.25036	1.72435	53.051
1.52245	0.80708	53.012
1.98802	1.58274	52.969
2.11371	1.11920	52.949
2.38139	1.26161	52.978
1.90285	1.00958	53.055
2.61847	1.38658	52.954
1.07347	0.56840	52.951
26.64828	14.11953	52.986

[1] This Journal, **20**, 119, February, *1898*.

Hence, if O = 16, H = 1.008, and Cl = 35.45, the atomic weight of zirconium becomes

90.78 in mean,
91.12 maximum,
90.61 minimum.

As further results are promised, this investigation is to be regarded as a preliminary research, rather than as a final determination.

THORIUM.

Brauner's work upon the atomic weight of thorium[1] has as yet appeared only in abstract. The determinations were made with the normal oxalate, in which thorium dioxide was estimated by heating, and the C_2O_3 was measured by titration with potassium permanganate. The values found for thorium with O = 16, were

232.50	232.33
232.46	232.50
232.45	232.44
232.31	232.35

In mean, Th = 232.42.

CERIUM.

Brauner's paper upon the compound nature of cerium,[2] has also only appeared in abstract. By a series of fractionations oxides were obtained giving atomic weights ranging from 140.25 down to 130.70. As the atomic weight decreases, the color of the oxide changes from white to reddish-brown orange. Brauner infers that cerium is accompanied by another metal of atomic weight about 110. Yttrium was looked for in the lower fractions, but not found, nor were there any lines in the spark spectra, other than those of cerium. The supposed new element, like gadolinium, may have no characteristic spectrum.

THE DIDYMIUMS.

Jones[3] has determined the atomic weights of neodymium and praseodymium by means of the synthesis of the sulphates from the oxides. The material for the investigation was furnished by Wal-

1 *Chem. News*, 77, 160, April 7, *1898*.
2 *Ibid.*, 77, 160, April 7, *1898*.
3 *Am. Chem. J.*, 20, 345, May, *1898*.

dron Shapleigh, and was very nearly pure. It was further purified by repeated fractional crystallizations of the double ammonium nitrates. From these salts the oxalates were prepared, and, from the latter, the oxides. The superoxide of praseodymium, Pr_4O_7, was reduced to Pr_2O_3 by ignition in hydrogen.

For praseodymium the results obtained were as follows, when O = 16 and S = 32.07 :

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0.5250	0.9085	140.42
0.6436	1.1135	140.50
0.7967	1.3788	140.38
0.7522	1.3018	140.38
0.7788	1.3473	140.53
0.6458	1.1172	140.54
0.6972	1.2062	140.51
0.7204	1.2464	140.49
0.8665	1.4990	140.54
0.6717	1.1624	140.40
0.7439	1.2873	140.42
0.6487	1.1224	140.47
8.4905	14.6908	140.46

With O = 15.88, Pr = 139.41.

For neodymium the data are as follows :

Weight Nd_2O_3.	Weight $Nd_2(SO_4)_3$.	Atomic weight Nd.
0.8910	1.5296	143.58
0.7880	1.3530	143.51
0.9034	1.5509	143.57
0.7668	1.3166	143.51
0.8908	1.5296	143.49
0.8848	1.5194	143.46
0.8681	1.4903	143.57
0.8216	1.4103	143.62
0.8531	1.4646	143.56
0.8711	1.4957	143.50
0.8932	1.5332	143.62
0.8893	1.5268	143.55
10.3212	17.7200	143.55

This value for neodymium must be corrected for the presence of a little praseodymium, which was estimated by the intensity of its lines in the spectrum. Corrected it becomes 143.6, or 142.52 when O = 15.88.

It is noteworthy that the values found by Jones almost absolutely reverse those given by von Welsbach, who puts praseodymium at 143.6 and neodymium at 140.8. Possibly the error in the latter figures may be only typographical.

Another determination of the atomic weight of praseodymium is due to C. von Schele,[1] who worked up 100 kilos of monazite to obtain his material for investigation. Two methods of determination were tried: one by synthesis of sulphate from oxide, the other based upon the oxalate. The oxide itself was prepared from the oxalate, and reduced from Pr_4O_7, or as v. Schele gives it, PrO_2, to Pr_2O_3, by ignition in hydrogen. Disregarding a preliminary series of experiments, made with impure material, and also the oxalate series, which gave unsatisfactory results, the final data are as follows:

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0.6872	1.1890	140.30
0.7834	1.3550	140.46
0.6510	1.1260	140.45
0.7640	1.3216	140.42
0.5183	0.8967	140.32
	Mean,	140.40

This value, computed with O = 16, and S = 32, is sensibly identical with that found by Jones.

In the case of neodymium a single determination of atomic weight has been published by Boudouard.[2] 2.758 grams of sulphate gave 1.605 of oxide, or 58.194 per cent. Hence, with O = 16 and S = 32, Nd = 143.045.

In this connection the spectroscopic work of Demarçay,[3] may also be properly noted. This chemist has studied the spectrum of neodymium obtained from diverse sources, and finds it to be definite and uniform. He therefore concludes that the metal is a distinct element, and not, as some chemists have thought, a mixture.

A preliminary notice, by Brauner,[4] of determinations of atomic weight upon the two metals in question, has also appeared. The material studied was obtained from Dr. Shapleigh, the

1 *Ztschr. anorg. Chem.*, **17**, 319.
2 *Compt. rend.*, **126**, 900.
3 *Ibid.*, **126**, 1039.
4 *Chem. News*, **77**, 161, April 7, *1898*.

determinations being made by the sulphate and oxalate methods. For praseodymium he obtained values ranging from 140.84 to 141.19, the average of thirteen determinations being Pr = 140.95.

Neodymium gave values from 143.4 to 143.63, but the material used still contained two and nine-tenths per cent. praseodymium. Here again Welsbach's figures are reversed.

MISCELLANEOUS NOTES.

In a series of papers Daniel Berthelot[1] shows that the true molecular weights of gases can be computed from their normal densities with the help of their coefficients of compressibility. By suitable mathematical formulas, from existing data, he computes the following values, taking O = 16 as his standard of comparison.

H = 1.0074.	
N = 14.005.	From N and N_2O.
C = 12.005.	From CO, CO_2, and C_2H_2.
A = 39.882.	
Cl = 35.479.	From HCl.
S = 32.046.	From SO_2.

From the density of nitrogen he finds N = 14.000; and from nitrous oxide, N = 14.007. These values he regards as superior to those determined by Stas, which are much higher; but Vêzes,[2] in a critical note, expresses the contrary opinion. After all, a mathematical discussion of data depends for its ultimate value upon the accuracy of the data, and an exact theory applied to inexact material may yield inferior results. It may well be asked, therefore, whether the experimental data discussed by Berthelot are superior to those furnished by the researches of Stas, and this is the real point at issue. So far, the work of Stas does not seem to be overthrown.

The paper by Dulk,[3] "Atomgewicht oder Atomgravitation," is essentially an abstract or summary of a book. Starting with H = 1, by a system of geometric configurations, the author computes a series of values for atomic weights, which are sometimes curiously near the experimental determinations. The following atomic weights are computed:

1 *Compt. rend.*, **126**, 954, 1030, 1415, and 1501.
2 *Ibid.*, **126**, 1714.
3 *Ber. d. chem. Ges.*, **31**, 1865, July 25, *1898*.

Li,	7.0	I,	126.23	Cu,	63.339
Na,	23.06	N,	14.0	Ag,	107.717
K,	39.111	O,	16.0	Au,	195.77
Rb,	84.96	F,	18.928	Hg,	198.45
Cs,	131.1	B	11.041	Zn,	65.385
Cl,	35.464	C,	11.9497	Cd,	112.0
Br,	79.666	Si,	28.0	Tl,	204.298

NEW TABLES.

Two new tables of atomic weights have appeared during the year; one by Richards,[1] the other by a committee of the German Chemical Society, consisting of Professors Landolt, Ostwald, and Seubert.[2] Both tables coincide in the main with that of your committee, but in some instances there are differences which can be eliminated only by new investigations.

Richards' table is preceded by a careful discussion of some points at issue, especially as regards the atomic weights of antimony, cadmium, calcium, magnesium, platinum, tungsten and uranium. For antimony, Richards prefers the value 119.92, or in round numbers 120, which depends on Cooke's analyses of the bromide, and involves the rejection of other data which seem entitled to some weight. For cadmium he accepts the higher value 112.3, rather than 112. Morse and Arbuckle's recent work lead me to adopt the value 112.38 for the present, bringing the committee table into harmony with that of Richards. In the case of calcium Richards regards the value 40.07 as too high, and adopts the round number 40. For magnesium, two values are in controversy, and here again Richards accepts the higher. In this case more evidence is needed. The same thing is true of platinum, tungsten, and uranium. The atomic weights of all three are uncertain to some tenths of a unit at least, and where Richards has selected data, I have preferred to use least square averages. New and better determinations are necessary in all three cases.

The committee of the German Chemical Society present their table without discussion of the data, so that it represents their careful judgment as to the best values for analytical use, unencumbered by argument. All three of the members, however, argue at length in favor of O = 16, as the basis of the scale, and give the well-known reasons in support of that view. Apart

[1] *Am. Chem. J.*, 20, 543, July, *1898*.

[2] *Ber. d. chem. Ges.*, 31, 2761, November 28, *1898*.

from theory, the oxygen scale certainly has the merit of greater convenience. The committee also suggest the desirability of an international commission upon atomic weights, and in that all chemists are likely to agree.

In the following table of atomic weight your committee give first its own sets of values, based upon both standards, H = 1, and O = 16. These values are only rounded off to the second decimal place, and represent, so far, the actual results of recalculation from the original data. Next is given Richards' table, and finally the table of the German Chemical Society, both sets of constants being more or less rounded off by the authors for convenience in practical use. It will be seen at once that the values adopted are in most cases sensibly identical. The new elements coronium, polonium, radium, monium, etherion, krypton, neon, xenon, and metargon are omitted, for lack of sufficiently precise data.

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Aluminum	26.91	27.11	27.1	27.1
Antimony	119.52	120.43	120.0	120.
Argon	?	?	39.9	40.
Arsenic	74.44	75.01	75.0	75.
Barium	136.39	137.43	137.43	137.4
Bismuth	206.54	208.11	208.0	208.5
Boron	10.86	10.95	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.54	112.38	112.3	112.
Caesium	131.89	132.89	132.9	133.
Calcium	39.76	40.07	40.0	40.
Carbon	11.91	12.00	12.001	12.00
Cerium	138.30	139.35	140.0	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.74	52.14	52.14	52.1
Cobalt	58.55	58.99	59.00	59.
Columbium	93.02	93.73	94.0	94.
Copper	63.12	63.60	63.60	63.6
Erbium	165.06	166.32	166.0	166.
Fluorine	18.91	19.06	19.05	19.
Gadolinium	155.57	156.76	156.0	....
Gallium	69.38	69.91	70.0	70.
Germanium	71.93	72.48	72.5	72.
Glucinum	9.01	9.08	9.1	9.1
Gold	195.74	197.23	197.3	197.2
Helium	?	?	4.0	4.
Hydrogen	1.000	1.008	1.0075	1.01

	Clarke.			
	R = 1.	O = 16.	Richards.	German.
Indium	112.99	113.85	114.0	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.66	193.12	193.0	193.
Iron	55.60	56.02	56.0	56.
Lanthanum	137.59	138.64	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.10	24.28	24.36	24.36
Manganese	54.57	54.99	55.02	55.
Mercury	198.49	200.00	200.0	200.3
Molybdenum	95.26	95.99	96.0	96.
Neodymium	142.52	143.60	143.6	144.
Nickel	58.24	58.69	58.70	58.7
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.55	190.99	190.8	191.
Oxygen	15.88	16.00	16.000	16.00
Palladium	105.56	106.36	106.5	106.
Phosphorus	30.79	31.02	31.0	31.
Platinum	193.41	194.89	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.41	140.46	140.5	140.
Rhodium	102.23	103.01	103.0	103.0
Rubidium	84.78	85.43	85.44	85.4
Ruthenium	100.91	101.68	101.7	101.7
Samarium	149.13	150.26	150.0	150.
Scandium	43.78	44.12	44.0	44.1
Selenium	78.58	79.17	79.0	79.1
Silicon	28.18	28.40	28.4	28.4
Silver	107.11	107.92	107.93	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.61	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.45	182.84	183.0	183.
Tellurium	126.52	127.49	127.5	127.
Terbium	158.80	160.00	160.0	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.87	232.63	233.0	232.
Thulium	169.40	170.70	170.0	....
Tin	118.15	119.05	119.0	118.5
Titanium	47.79	48.15	48.16	48.1
Tungsten	183.43	184.83	184.4	184.
Uranium	237.77	239.59	240.0	239.5
Vanadium	50.99	51.38	51.4	51.2
Ytterbium	171.88	173.19	173.0	173.
Yttrium	88.35	89.02	89.0	89.
Zinc	64.91	65.41	65.40	65.4
Zirconium	89.72	90.40	90.5	90.6

NOTE.

Drown's Method of Determining Silicon.[1]—In the July number of this Journal, George Auchy has described a method devised by him, which will effect a more thorough dehydration of the silica than is obtained by the method usually followed. Dr. Dudley[2] called attention to the difficulty of dehydrating in this case at the Troy meeting of this society in 1896.

Without claiming any superiority over Mr. Auchy's method it may be of interest to describe a modification which has been in use in this laboratory for a number of years. It is not original with the author.

The pig iron or steel is weighed into a No. 4 beaker and brought into solution by the usual method as described by Blair. We then add forty cc. of concentrated sulphuric acid and evaporate to fumes on the hot plate. A leather strap about one inch broad and twenty inches long is passed under the lip of the beaker and the ends clasped between the thumb and forefinger. By a slight wrist movement the contents of the beaker are given a rapid rotary movement. The beaker can, in this way, be heated directly in the full flame of the Bunsen burner with perfect safety. Care only must be taken that the contents are kept in continual motion and that sufficient acid is present to cover the glass exposed to the flame. Under these circumstances any lumps are broken up and a thorough contact between the silica and the very hot acid is insured. In many other cases where evaporation to fumes is necessary and the tendency to bump prevents the simple boiling down of the solution, the use of a strap in this way is invaluable. As a rule, it will be found more convenient than the use of the casserole. It is also very convenient in handling hot beakers as it is adaptable to one of any size.

We perhaps run the risk of recounting what may be to some chemists an old story, but, as in our experience we have yet to visit a laboratory in which the strap was used in this way, it is but reasonable to conclude that it has not met with the attention it deserves.

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NEW YORK.

[1] This Journal, 20, 547.
[2] *Ibid.*, 19, 106.

BOOKS RECEIVED.

Commercial Organic Analysis. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicines, with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.S.C., F.C.S. Third Edition, Illustrated. With revisions and addenda by the author and Henry Leffmann, M.A., M.D. Volume II.—Part I.—Fixed Oils, Fats, Waxes, Glycerol, Nitroglycerin and Nitroglycerin Explosives. Philadelphia: P. Blakiston's Son & Co. 1899. x+371 pp. Price, $3.50.

Fish as Food. By C. F. Langworthy, Ph.D. Farmer's Bulletin, No. 85, U. S. Department of Agriculture, Washington, D. C. 1898. 30 pp.

Grasses, Clovers, Forage, and Economic Crops. By W. R. Dodson and Wm. C. Stubbs. Bulletin No. 53, Second Series, of the Agricultural Experiment Station of Louisiana State University and A. and M. College, Baton Rouge, La. 55 pp. and several plates.

Vinegar Adulteration and the Extent to Which It Exists in the Samples for Sale in North Carolina. Bulletin No. 153, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 8 pp.

The Adulteration of Coffee and Tea Offered for Sale in North Carolina. Bulletin No. 154, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 16 pp.

Electrolysis and Electrosynthesis of Organic Compounds. By Dr. Walther Löb. Authorized Translation by H. W. F. Lorenz, A.M., Ph.D. New York: John Wiley & Sons. 1898. xiii+103 pp. Price, $1.00.

Ninth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky for the Year 1896, containing also Bulletin No. 61 (Potatoes), Bulletin No. 62 (Strawberries), Bulletin No. 63 (Tobacco), Bulletin No. 64 (Analyses of Commercial Fertilizers), and Bulletin No. 65 (Analyses of Commercial Fertilizers). Kentucky Agricultural Experiment Station, Lexington, Ky. 1898. xliii+114 pp.

An Introductory Course of Quantitative Chemical Analysis, with Explanatory Notes and Stoichiometric Problems. By Henry P. Talbot. Third Edition, Revised and Enlarged. New York: The Macmillan Co. 1899. 153 pp. Price, $1.50.

Lavas and Soils of the Hawaiian Islands. Investigations of the Hawaiian Experiment Station and Laboratories. Walter Maxwell, Director and Chief Chemist. Honolulu: The Hawaiian Sugar Planters' Association. 1898. 186 pp.

Text-book of Medical and Pharmaceutical Chemistry. By Elias H. Bartley, B.S., M.D., Ph.G. Fifth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1898. xiv+738 pp., with 96 illustrations. Price, 3.0 .